CHALMERS
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Chemical Systems Used in Specialty Cleaning Formulae

Understanding of Bulk Properties for Enhanced Chemical Paint Stripping

Master's thesis in Materials Chemistry and Nanotechnology

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Gothenburg, Sweden 2015

MASTER'S THESIS 2015

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Cover: Paint stripping caused by the application of chemical paint stripper on the surface of a painted tile strip, see page 13 regarding paint stripping tests for further information.

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ABSTRACT

Chemical paint stripping is among the most gentle paint removal techniques available for industrial paint stripping, since it can remove the paint while preserving the substrate. Formulations that are water-based can be more environmentally friendly than their solvent-based counterparts, especially with a careful selection of surfactants and additives. In this Master thesis project a detailed study of one water-based paint stripper has been carried out to gain understanding of the bulk properties of the system, in order to find effective ways to improve the product with regard to stripping efficacy and environmental impact. The investigated system is composed of an ionic surfactant, an aromatic alcohol, an additive (a weakly basic organic electrolyte) and water, and it was studied using surface tension, conductivity and NMR spectroscopy. The effect of altered compositions of surfactant and electrolyte, as well as substitution of surfactant or electrolyte with other species, on the phase diagrams was also studied and the different systems paint stripping efficacy was tested.

The studies indicate that the system forms a microemulsion, and several of the results points toward that the aromatic alcohol (constituting the oil phase of the emulsion) acts as a co-surfactant, where it lowers the CMC and increases the degree of ionization of the micelles in the formulation. The additive of the studied system is found to have an enhancing effect on the paint stripping efficacy of the product, which may be caused by the alkaline nature of the additive. The results also indicate that the additive amplifies the effects of the solvent on the system, such as further decreasing the CMC and increasing the degree of ionization, however weakly. Decreasing the concentration of additive, as well as complete substitution with a similar substance, had a deteriorating effect on the paint stripping efficacy of the formulation. Partial substitution of the ionic surfactant for non-ionic sugar based hydrotropes is found to give comparable paint stripping efficacy as the original formulation, and to only cause minor changes in the phase diagram.

Keywords: Paint stripping, Paint removal, Emulsion, Anionic surfactant, Aromatic alcohol, Co-surfactant, Surface tension, Conductivity, NMR, Self-diffusion

ABBREVIATIONS

A1	Additive used in EnviroStripp’s formulation, a weakly basic (short) water-soluble organic molecule
A2	Additive investigated as replacement for A1, a strong basic organic molecule with similar functional groups as A1
CMC	Critical Micelle Concentration
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
NOESY	Nuclear Overhauser Effect Spectroscopy
PGSE	Pulsed-Gradient Spin-Echo
RT	Room temperature
S1	Surfactant used in EnviroStripp’s formulation, short chained anionic surfactant
S2	Surfactant investigated as replacement for S1, a non-ionic surfactant with a broad size distribution range
S3	Surfactant investigated as replacement for S1, a non-ionic surfactant with a narrow size distribution range
S4	Surfactant investigated as replacement for S1, a short chained sugar-based non-ionic surfactant
S5	Surfactant investigated as replacement for S1, a short chained sugar-based non-ionic surfactant similar to S4 but with a larger tail group
wt%	Weight percent

TABLE OF CONTENTS

1. Introduction 1
  1.1. Purpose and aim 2
2. Theory 3
  2.1. Surfactants in aqueous solutions and emulsions 3
    2.1.1. Dispersed systems 5
    2.1.2. Co-surfactants, co-solvent and hydrotropes 5
    2.1.3. Alcohols as co-surfactant in micellar systems 5
  2.2. Water based paint removal systems 7
    2.2.1. Stripping mechanism 7
  2.3. Analysis methods 7
    2.3.1. Ternary phase diagrams 7
    2.3.2. Tensiometry 8
    2.3.3. Conductivity 9
    2.3.4. NMR spectroscopy 10
3. Experimental procedure 13
  3.1. Ternary phase diagrams 13
    3.1.1. Paint stripping test 13
  3.2. Surface tension measurements 14
  3.3. Conductivity measurements 14
  3.4. NMR spectroscopy 14
  3.5. pH analysis 14
4. Results and discussion 15
  4.1. Phase diagrams 15
  4.2. Paint stripping 17
  4.3. Physicochemical studies of the bulk properties 20
    4.3.1. Determination of CMC 20
    4.3.2. Micellar properties 22
    4.3.3. Influence of the different components on the system 27
5. Conclusions 30
6. Future work 31
7. Acknowledgements 32
8. References 33

Appendix i
I. Ternary phase diagrams i
II. Surface tension measurements and fitting of Gibbs equation iii
III. Surface tension measurements and fitting of the Langmuir equation viii
IV. Conductivity xii
V. Diffusion xv

1. INTRODUCTION

Industrial paint removal, or paint stripping, is a demanding area in industry since it often requires removal of paint in a safe and efficient way, without impairing the quality of the underlying surface or part. If imperfections in the paint layer occurs during production it is often more profitable to strip the paint and redo the work than to dispose of the whole part, and there will also be a need of removing excess paint from the racks that support the parts during painting [1]. When the paint stripping will be performed repeatedly, such as for the support racks, it is especially important to use a gentle stripping process that minimizes the damage of the underlying material.

There are three main categories of paint removal processes; mechanical, physical, and chemical. Mechanical processes consist of methods such as grinding, sanding and shaving, while physical processes often use heat for example in the form of infrared radiation or hot air. The mechanical methods produce dust particles and are, along with the heating methods, often rough on the surface the paint is removed from [2, 3, 4]. Chemical paint removal, on the other hand, can remove the paint selectively and can thus be a gentler alternative compared to the other methods [5].

Chemical paint stripping works by two main mechanisms; it can dissolve the paint, or cause the paint to swell and flake by weakening the bonds between the paint and the substrate (i.e. the surface it was adhered to) [6]. Dissolution of the paint is undesirable in industrial processes since it often causes redepositioning of the paint, while at the same time complicating the separation of the paint from the stripper. Flaking of the paint from the substrate is facilitated by decreasing the adhesion between the substrate and the paint film and is achieved by the solvent penetrating between the paint and the substrate.

Traditionally chemical paint stripping products consist of a solvent along with a number of facilitating substances, such as co-solvents. For the purpose of swelling the paint rather than dissolving it completely, dichloromethane (DCM) was for a long time viewed as a great solvent for paint stripping. After DCM the more advantageous N-methyl pyrrolidone (NMP) became common in paint stripping formulations partly because it is non-cancerogenic and causes no readhesion of paints [7]. Acid and alkali paint strippers are other types of chemical strippers which are not as sensitive to the pigment content or thickness of the paint film for the paint removal process [8]. Strongly alkaline lye has been one of the most commonly used chemical paint stripper in industry [8]. But due to both health- and environmental concerns research has been conducted in the last decades to develop less harmful alternatives [4]. One new type of paint stripping product that has emerged utilizes water based formulations, where surfactants are introduced both to make the solvent and water miscible and to facilitate flaking of the paint. The surfactant lowers the interfacial tension between the liquid and the substrate, and also between the liquid and the paint film, thereby making it more energy efficient for the system to separate the paint from the substrate i.e. it lowers the adhesion between them [9]. A conversion to water based stripping products can greatly reduce the amount of solvent, which gives great environmental benefits, but at the same time the introduction of surfactants raise a new set of environmental issues that need to be addressed. A careful selection of surfactant is required to minimize the environmental impact of the new formulation, and at the same time the product quality and paint removal efficiency must be maintained, or improved, to keep a good position on the market.

While environmental aspects are of high importance, these new water based systems also raise a new set of questions with respect to their paint removal mechanisms. Water based paint stripping products does already exist on the market [10, 11], but the main mechanisms behind their functions are not always known [5]. There are two intuitive ways to envisage the paint removal process of a water/surfactant/solvent system; one is that the water and surfactant only form a carrying system that still allows the solvent to reach the paint and do its job in the same manner as when only solvent is applied [5], and the other is based on the fact that water/surfactant/oil systems are already known for their great cleaning abilities [12, 13] which opens up for a discussion on whether the surfactant is also actively helping or facilitating the paint removal process. Since the system consists of water, surfactant and an (organic) solvent, it is often possible for the components to form an emulsion or possibly a micro-emulsion, and thus to have several roles.

In this project an investigation of a water based paint stripping product will be performed in order to further deduce the system properties and paint stripping mechanisms of the formulation, especially with respect to the role of the surfactants. With proper knowledge on each components function, further optimizations can also be carried out both in regards to efficiency as well as with respect to minimizing environmental impact.

1.1. PURPOSE AND AIM

This thesis work is a continuation of the thesis work carried out by Kim Andersson [14] where two stripping systems used in paint (i.e. polymeric film) removal were studied. In this continuing thesis a more elaborated study of one of those systems is carried out. The studied system is a cold stripping system, meaning that it is used at room temperature (RT).

The purpose of this thesis work is to find improvements to the stripping product to make it more environmentally friendly without compromising the paint removal efficiency. Thus changes that leads to a product with lower environmental impact, and not just improved stripping efficacy, are seen as improvements of the formula. Examples of improvements are; decreasing the amount of surfactant, solvent or additive along with replacing the surfactant/additive with a less harmful substitute.

The aim of this master thesis is to study the bulk properties of the cold stripping system. The ambition is to gain a better understanding of how the surfactant, solvent and additive affect the system properties and the performance of the product. To fulfil this aim, the focus is directed towards answering a few fundamental questions about the system. Experimental work is carried out to determine whether the formulation is a microemulsion, and also to determine the individual roles of the surfactant, solvent and additive in the system. Investigations with altered product compositions are made in order to determine whether some of the surfactant can be replaced with other biodegradable surfactants, whether the amount of additives can be decreased or if some additive can be replaced, and if the paint removal efficiency of the product is maintained (or improved) with these altered compositions. Due to multiple interactions between the components at high concentration the more detailed studies of the bulk properties are done at considerably lower concentrations than the phase diagram and paint stripping tests which are carried out at concentrations close to the composition of EnviroStripp’s product.

2. THEORY

The theoretical background relevant for this project is presented in the following sections, starting with a description of the significant surfactant properties, which is followed by an explanation of water based paint removal systems, and lastly a short explanation of the analysis methods used during the project.

2.1. SURFACTANTS IN AQUEOUS SOLUTIONS AND EMULSIONS

Surfactants are amphiphilic molecules, i.e. they consist of a polar (hydrophilic) head group and a nonpolar (hydrophobic) tail, see Figure 1. Since the two ends prefer different environments, they adsorb at interfaces between phases of different polarity, such as oil and water. There they can lower the total free energy of the system by positioning the polar head in water, while putting the tail in the more suitable oil phase. There is an equilibrium between the surfactants adsorbed at interfaces and the surfactants dissolved in the liquid as unimers, and at the critical micelle concentration (CMC) the surfactants will also start to form aggregates since this lowers the total energy of the system [15, 16]. In aqueous solution the aggregates, also called micelles, consist of a core where the hydrophobic tails interact with each other, while the outer surface of the micelle is covered in polar groups that interact more favourably with the water phase. The onset of formation of micelles occurs at the critical micelle concentration, which is individual for each surfactant system since it depends on the unimer solubility [15]. A low CMC indicates low solubility of the unimer, and thus a greater driving force to form aggregates.

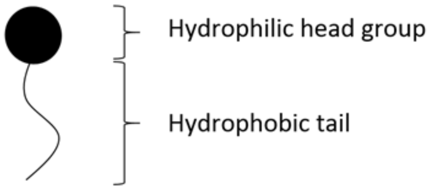

FIGURE 1. SCHEMATIC PICTURE OF THE DIFFERENT PORTIONS OF A SURFACTANT.

Surfactants are often categorized based on their head group properties, as can be seen in Figure 2. Micelle formation has a significant impact on the physical properties of the solution, see Figure 3, and the CMC is both structure-dependent as well as influenced by surrounding factors. A charged head group results in higher CMC than for non-ionic surfactants, and an increased alkyl chain length has a depressing effect on the CMC [17]. Increased temperature decreases the CMC of many non-ionic surfactants, but has little effect on ionic surfactants, while addition of salt dramatically lowers the CMC of ionic surfactants only, leaving non-ionic surfactants unaffected [17]. For short chained surfactants, that associate weakly, different methods of determining the CMC can give somewhat different values of the CMC [17].

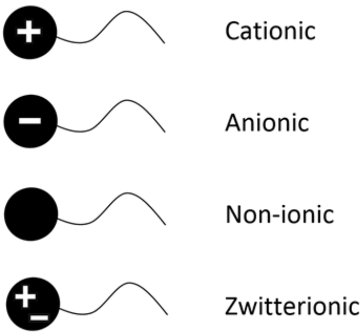

FIGURE 2. SURFACTANT CATEGORIZATION BASED ON HEAD GROUP CHARGE.

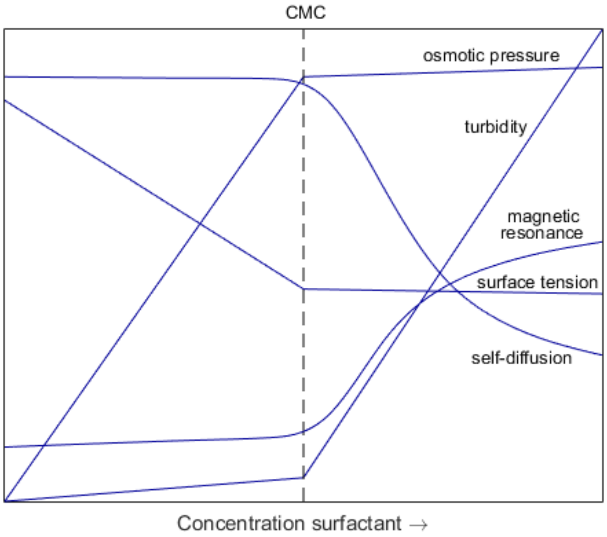

FIGURE 3. ILLUSTRATION OF THE DEPENDENCE OF SOME PHYSICAL PROPERTIES ON SURFACTANT CONCENTRATION [17].

The shape and size of the micelles depend on the packing parameter and the length of the hydrophobic part. Since the micelle core cannot be hollow, the smallest dimension (i.e. the diameter in a sphere, or the shortest cross-section dimension in rods or ellipsoids etc.) of a surfactant in aqueous solution cannot exceed a size of two times the length of the hydrophobic tail [18]. The packing parameter, P, can be calculated according to Equation 1.

$$P = \frac{V_H}{l_c a_0} \qquad \textbf{Eq. 1}$$

where V_H is the volume of the hydrophobic group, l_c is the length of the hydrophobic tail, and a_0 is the cross-sectional surface area occupied by the hydrophilic group at the micelle-water interface [19]. It can be interpreted as a factor describing the shape of the surfactant, low values indicating a cone-like shape, and values close to 1 indicating surfactants that resemble a cylinder. The shape of the unimer has a substantial impact on the structure of the micelle, conical unimers giving spherical micelles, and cylindrical unimers preferring lamellar phases due to the curvature that the shape of the surfactants induces when packing together [19], see Figure 4. The head group surface area, a_0, is larger for ionic surfactants than non-ionic, due to the repulsion between the equal charges. Since a micelle gathers a large amount of charge in a small volume, counterions will concentrate close to the micelle surface to neutralize the charge. The counterion binding can be observed by calculating the degree of ionization, which is a fractional value comparing the net charge of the micelle to the (theoretical) micelle charge without the presence of counterions [20].

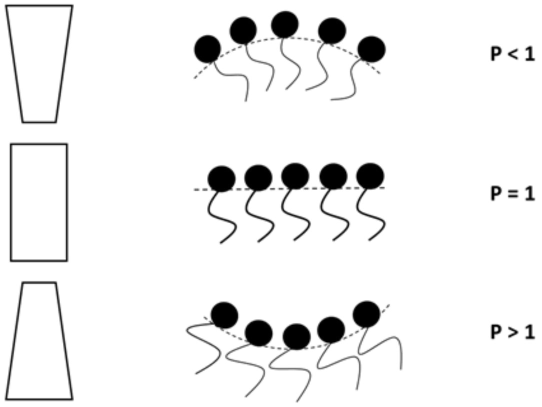

FIGURE 4. SCHEMATIC PICTURE OF DIFFERENT PACKING PARAMETERS AND THE DIFFERENT AGGREGATE CURVATURE THEY INDUCE.

2.1.1. DISPERSED SYSTEMS

Mixing of two different liquids can give three different outcomes. If the liquids are fully miscible a single phase is formed, but if they are not fully miscible a two phase system is created. A two phase system could consist of an emulsion or a microemulsion, which are both composed of a dispersion of one liquid phase in another liquid phase. Emulsions and microemulsions are often formed with the help of surfactants, which are great emulsifiers due to their amphiphilic properties, and can lower the interfacial tension between the two immiscible liquids, thus allowing an increased interfacial area and making smaller dispersed droplets possible [15].

Despite the similarities, there are fundamental differences between emulsions and microemulsions. Emulsions consist of larger droplets than microemulsions, and will eventually phase separate since they are not thermodynamically stable [21]. They also require applied force to form droplets, which are not very dynamic in nature. On the contrary, microemulsions are thermodynamically stable, can form spontaneously, and consist of much smaller droplets (around 10 nm in diameter) in a highly dynamic system [21]. The difference in droplet size leads to a larger interfacial surface area in microemulsions compared to macroemulsions. Surfactants are often used to decrease the interfacial tension between the two immiscible phases to allow a larger contact area, and wile emulsions can form without surfactants, microemulsions require at least one surfactant, often together with a co-surfactant, to form [21].

2.1.2. CO-SURFACTANTS, CO-SOLVENT AND HYDROTROPES

Co-surfactants are weakly amphiphilic molecules that do not self-assemble by themselves, but strongly promote aggregation of the primary surfactant [22]. They contribute to the surfactant effects on the system by further reducing the surface tension, and by co-adsorbing at the interfaces they change the overall packing parameter [23], which also induces a change in the curvature of the interface where the surfactants are situated and thus in extension affects the size of the aggregates.

One way to improve the solubility of poorly soluble substances in water without using a surfactant is to add a co-solvent [24]. Co-solvents are fully miscible with water, and thus the addition changes the properties of the bulk which increases the solubility of the poorly soluble substances [25]. Co-solvents are not necessarily amphiphilic but can still lower the interfacial tensions of the system [22].

Another type of weak amphiphilic molecules that has a lowering effect on the surface tension are hydrotropes [26]. True hydrotropes do not self-associate in water, and thus an aqueous solution of a hydrotrope does not exhibit the distinct break in the surface tension versus concentration plot characteristic for surfactants [26]. Their behaviour is somewhere in between a co-solvent and a surfactant, and they can often help lower the CMC of surfactants by acting like a co-surfactant [26].

2.1.3. ALCOHOLS AS CO-SURFACTANT IN MICELLAR SYSTEMS

Besides the function as organic solvent, the amphiphilic properties of alcohols also open up for other interactions in micellar systems. The effects of alcohol on surfactant behaviour in aqueous solution vary greatly based on the type of alcohol and surfactant. Short-chained alcohols are water soluble due to their polarity, while long chain alcohols have properties more similar to those of nonpolar organic molecules [27]. The hydroxyl group in combination with an aliphatic chain also give the alcohol amphiphilic properties. In an aqueous surfactant solution, the alcohol can be distributed between three energetically different sites; the aqueous phase, the palisade layer near the micelle surface (illustrated in Figure 5), and the core of the micelle [27].

Short chained alcohols are water soluble, and could thus be viewed as predominantly co-solvents rather than co-surfactants [28, 29]. They are believed to decrease the cohesive energy density of the water, thus making the surfactant monomers more soluble and causing an increase in the CMC [20, 29]. As the chain length increases, it becomes more energetically favourable for the alcohol to assume a position within the more hydrophobic micelle, making the effect on the system more co-surfactant-like [28]. Medium-length alcohols are usually positioned in the palisade layer, close to the micelle-water interface, which causes them to have a large effect on the micelle properties [20, 28]. A significant decrease in the CMC can be observed as an effect of this, resulting in a minimum in CMC when the chain length of the alcohol is close to that of the hydrophobic tail of the surfactant [20]. Long chained, less polar alcohols, tend to reside within the core of the micelle, having only a slightly decreasing effect on the CMC [20].

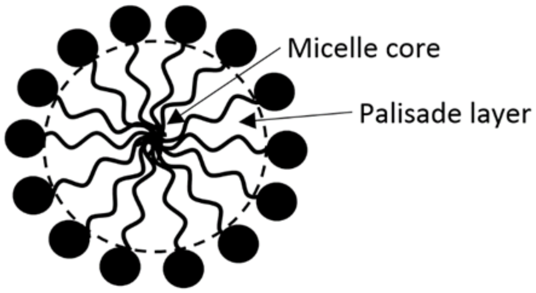

FIGURE 5. SCHEMATIC PICTURE ILLUSTRATING THE CORE AND PALISADE LAYER OF THE MICELLE.

The shape and number of polar groups on the alcohol also affects the co-surfactant properties. A bulky alcohol will experience a larger lateral pressure when residing at the palisade layer, which forces these molecules inwards towards the core of the micelle [20]. Since this pressure increases with increasing cross-sectional area of the molecule, bulky alcohols show less significant effects on the CMC compared to straight chained alcohols of the same size [20]. A larger number of polar groups will, on the other hand, bring the alcohol closer to the micelle-water interface, and thus have a larger effect on the CMC [20].

Regarding the influence of alcohols on micellar size, conclusions of different content can be formulated. Holmberg et al. [30] states that alcohols and other substances that reside in the outer part of the micelle has a general trend of increasing the size of the micelles. Moreira and Firoozabadi [28] on the other hand have concluded that medium length aliphatic alcohols residing in the palisade layer have a strong decreasing effect on micellar size. Another study on an ionic surfactant [27] observed completely different effects on size and shape of the micelles depending on the type of alcohol added to the system. Thus, it is hard to predict the effect on the micelles of introducing a specific alcohol to an aqueous surfactant system.

Some alcohols, such as 1-butanol and ethanol, are also capable of forming short-lived aggregates on their own in water [29, 31], with similarities to micelles, which is a factor that further complicates the prediction of their effect on surfactant systems.

When the alcohol acts as a co-surfactant in aqueous solution the aggregates formed can be viewed as mixed micelles. To investigate the distribution of the alcohol in the system, Perez-Villar et al presents a model to calculate the mole fraction of alcohol in the micelle based on the relative mole fractions of surfactant and alcohol in the solution [32]:

$$x_m^2 = x'_2 \cdot \delta \frac{CMC \cdot M_w - x'^2_1 \cdot D}{x'_1 \cdot (1 + x'_1 x'_2) \cdot D \cdot (1 - \delta) + \delta \cdot CMC \cdot M_w} \qquad \textbf{Eq. 2}$$

x^2_m being the mole fraction of alcohol within the micelle, and x' with index 1 and 2 denoting the mole fraction of surfactant and solvent respectively in the solution. x'_1 and x'_2 can be calculated by Equation 3, where n^0 with index 1 and 2 is the moles of surfactant and alcohol respectively in the solution. The number of ions created when one surfactant is dissociated is described by δ, M_w is the molecular weight of water, and D is the derivative of the logarithm of the CMC as a function of x'_2.

$$x'_1 = \frac{n_1^0}{n_1^0 + n_2^0} \;\; ; \;\; x'_2 = 1 - x'_1 \qquad \textbf{Eq. 3}$$

The model presented by Perez-Villar is based on an earlier thermodynamic model for mixed micellar systems containing two different surfactants. In their report [32] they develop this model further to include mixed micelles containing a surfactant and a self-aggregating alcohol, which they use to study the distribution of 1-butanol in mixed micelles with the ionic surfactant SDS (Sodium dodecyl sulfate).

2.2. WATER BASED PAINT REMOVAL SYSTEMS

A wide range of water based paint stripping formulations have been developed to answer the demand of replacements to the harmful solvents used on the market. There are reports of both water-in-oil [10] and oil-in-water [33] emulsions for the use in chemical paint removal, as well as other un-characterized systems with water as a major constituent [11]. The reoccurring components, besides water, are one or several organic solvents, often (but not always) together with a surfactant and a thickener of some sort [10, 11, 33]. Typical solvents include aromatic compounds, esters, alcohols, and other polar solvents [10, 11, 33], and the water content can be as high as 50-70 wt% [10, 11].

2.2.1. STRIPPING MECHANISM

Microemulsions are commonly used in cleaning for industrial applications, where the typical detergency mechanisms of classical binary micellar solutions for removal of oily soil include rolling up, emulsification and solubilisation [5, 12, 13]. Since the polymer film is not dissolved during paint removal the only mechanism correlating to the cleaning mechanisms of surfactants when using a microemulsion paint remover is the lowering of the interfacial tension between liquid-paint and liquid-substrate, which facilitates flaking of the film. For the removal of a polymer film with a solvent the mechanisms differ and consist of swelling and subsequent flaking, caused by the lowered adhesion when the solvent have penetrated between the film and the substrate along with the swelling of the polymer film [34, 35]. In classic solvent-based paint strippers surfactants are often used to penetrate between the paint and substrate, thus enhancing the paint removal efficiency [4]. In water based paint strippers, the primary functions of surfactants are to increase the wetting of the paint surface and to enable the formation of a system that can disperse the solvent. Co-solvents and co-surfactants are often added to increase the stripping efficacy of paint removal formulations by altering the physical properties of the system [4].

2.3. ANALYSIS METHODS

The following sections provide a short description of the analysis methods used in this project to evaluate the properties of the studied paint stripping system.

2.3.1. TERNARY PHASE DIAGRAMS

A ternary phase diagram is often used to graphically represent a three-component surfactant system at constant temperature and pressure [21], see Figure 6. Each vertex in the equilateral triangle represents one of the pure components water, oil or surfactant. A point on the opposing catheter of a vertex represents a binary mix of the other two components whereas a point inside the triangle represents a ternary system with all three components.

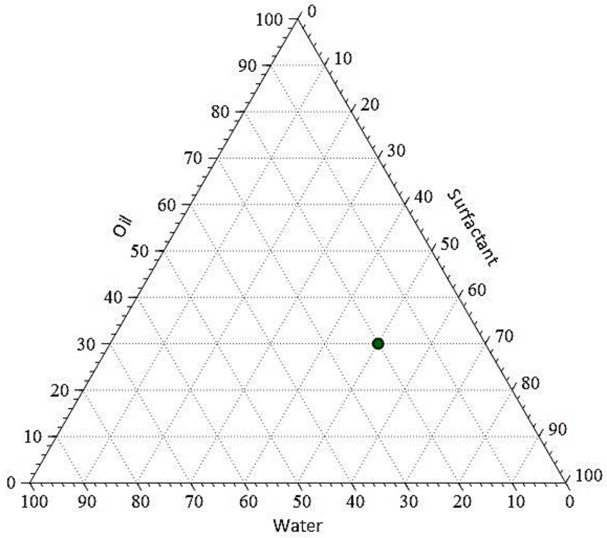

FIGURE 6. AN EXAMPLE OF A TERNARY PLOT OF A SAMPLE WITH COMPOSITION 20 WT% WATER, 50 WT% SURFACTANT AND 30 WT% OIL.

2.3.2. TENSIOMETRY

Tensiometry is used to determine the interfacial tension between two immiscible liquids or the surface tension of a liquid. There are a lot of methods available for measuring the surface tension of a liquid (or solution), ranging from optical tensiometry to max drop volume tensiometry to force tensiometry, where force tensiometry is the most commonly used method [36, 37]. The two main methods in force tensiometry are the Wilhelmy plate method and the du Noüy ring method [38].

In the du Noüy method a thin platinum ring is dipped into the liquid and held parallel to the surface. The ring is then slowly pulled up from the surface during which the force required to lift the ring is measured, and the maximum of the force along with the radius of the ring is used to calculate the surface tension of the liquid [39].

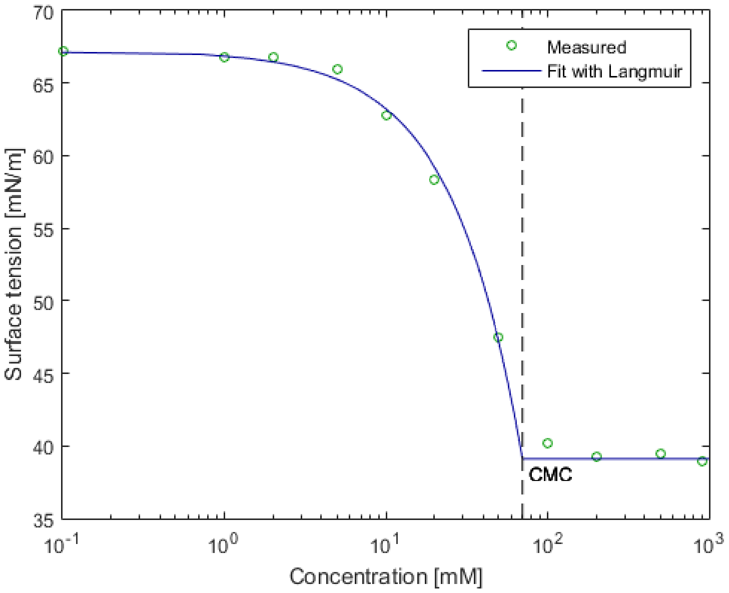

FIGURE 7. DETERMINATION OF CMC FROM THE PLOT OF SURFACE TENSION AGAINST CONCENTRATION OF SURFACTANT.

The critical micelle concentration (CMC) in a surfactant dispersion can be determined through surface tension measurement. The free surfactant unimers will go to the surfaces to lower the surface tension, while the surfactants aggregated into micelles do not contribute to the surface activity [30]. Below the CMC all surfactants added are dissolved as unimers, which affect the surface tension, while above CMC all additional surfactant added will aggregate into micelles making the concentration of unimers, and thus the surface tension, constant. As a result the CMC can be determined by plotting surface tension against surfactant concentration, giving the CMC value where the curve has a kink and becomes flat [40], see Figure 7.

The correlation between surfactant concentration and surface tension can also be used for Gibbs and Langmuir fittings, where additional properties of the surfactant system can be calculated.

2.3.2.1. GIBBS EQUATION

The concentration of surfactant at the interface can be calculated using Gibbs equation and is obtained from the slope of γ plotted versus $log\ C_1$, where n is the number of solute species which have a concentration at the interface that changes with change in C_1 [41]. For a 1:1 ionic surfactant (S^-X^+ or S^+X^-) in the presence of an abundance of electrolytes that have small and non-amphiphilic ions, or for a dilute solution of a non-ionic surfactant, n will be one [41]. For 1:1 ionic surfactants in the absence of electrolytes or other solutes, n will be equal to two [41].

$$\Gamma_1 = -\frac{1}{2.303 \cdot n \cdot R \cdot T}\left(\frac{\delta\gamma}{\delta log C_1}\right) \qquad \textbf{Eq. 4}$$

Γ_1 can then be used to calculate the surface area per adsorbate molecule on the adsorbent, a_1^s, in square Ångström

$$a_1^s = \frac{10^{16}}{N \cdot \Gamma_1} \qquad \textbf{Eq. 5}$$

where N is Avogadro's number [41]. This calculated a_1^s is also the same area as the one denoted a_0 in calculations of the packing parameter (Equation 1).

2.3.2.2. LANGMUIR-SZYSZKOWSKI EQUATION

The Langmuir-Szyszkowski equation, Langmuir for short, can just like Gibbs equation be used to calculate the concentration of surfactant at the interface (in systems with non-ionic surfactants, or where the ratio of ionic surfactant to counterion is 1:1) [42, 41]. But unlike the Gibbs equation, the Langmuir equation is fitted to the entire surface tension plot (up to the CMC).

$$\gamma = \gamma_0 - 2.303 \cdot R \cdot T \cdot \Gamma_m \cdot log\left(\frac{C_1}{a} + 1\right) \qquad \textbf{Eq. 6}$$

γ_0 is the surface tension of pure water (water + solvent), C_1 the bulk concentration of the surfactant and a is a constant. Γ_m is the maximum surface concentration of the surfactant (at monolayer adsorption) and is equal to Γ_1, from Equation 4, just below the CMC [41].

2.3.3. CONDUCTIVITY

Conductivity can be used to determine the CMC of ionic surfactant solutions, since addition of surfactant below the CMC causes an increase in number of charge carriers, from both the charged surfactant and its counter ion, which consequently increases the conductivity. Addition of surfactant above the CMC will only increase the concentration of micelles, which are less mobile and thus inferior charge carriers, while the unimer concentration remains constant. Additionally some of the counter ions will bind to the micelles to lower their surface charge density. This leads to a lower amount of added effective charge carrier when adding a given amount of surfactant above the CMC compared to below the CMC. This will cause a break in the curve when plotting conductivity against surfactant concentration from which the CMC can be determined, see Figure 8 [20, 43].

The degree of ionization, α, can be determined from the ratio between the two slopes by

$$\alpha = \frac{s_2}{s_1} \quad \textbf{Eq. 7}$$

where s_2 is the slope above the CMC, and s_1 is the slope below the CMC. Furthermore the degree of binding of the counterion to the micelle is found as

$$degree\ of\ binding = 1 - \alpha \quad \textbf{Eq. 8}$$

and thus it can be derived that a larger difference between the two slopes indicates a lower degree of ionization, which means a larger degree of binding of the counterion to the micelle.

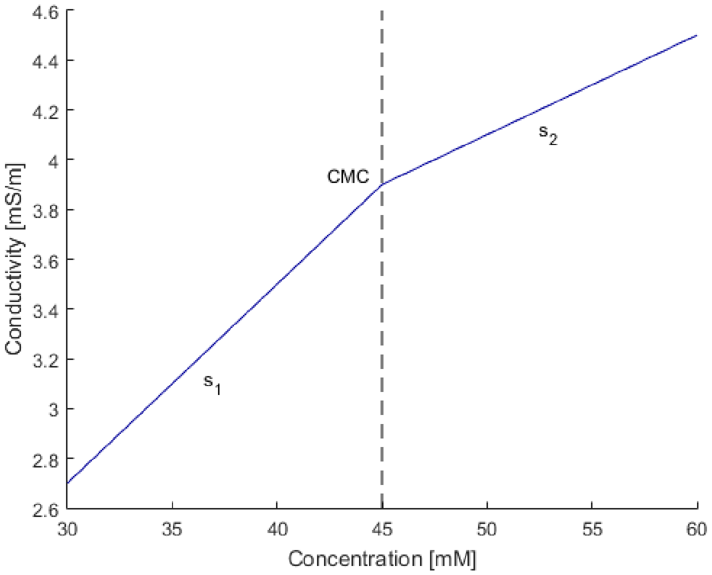

FIGURE 8. DETERMINATION OF CMC FROM THE PLOT OF CONDUCTIVITY AGAINST CONCENTRATION OF A SURFACTANT SOLUTION.

2.3.4. NMR SPECTROSCOPY

Nuclear Magnetic Resonance (NMR) spectroscopy is a technique used primarily to study molecular structure and it is based on the magnetic behaviour of the intrinsic spin properties in atomic nuclei (often hydrogen and carbon). NMR spectroscopy gives information about the number of magnetically distinct atoms and the immediate surrounding of the type of nuclei being studied [44]. By various NMR methods a range of different properties with respect to structure, dynamics, and interactions can be studied.

2.3.4.1. ONE-DIMENSIONAL ^{1}H NMR

The chemical shift of the surfactant signals in one-dimensional ^{1}H NMR spectra at a range of surfactant concentrations, below and above the CMC, can be used to determine the CMC of the system [45]. This can be accomplished since the chemical environment of the surfactant in micelles are different from the environment for unimers in solution and thus provides a different chemical shift.

2.3.4.2. PGSE

The self-diffusion of molecules can be studied using an NMR method based on Pulsed-Gradient Spin-Echo (PGSE) [46]. A pulsed radio frequency aligns the nuclear spins of the hydrogen atoms in a phase coherence, which is followed by a defocusing magnetic field gradient pulse that differ with position along the NMR tube, with the effect that the spin is equipped with a spatially position-dependent phase [47, 48]. After a time delay, the so-called diffusion time, a second radio frequency pulse is applied to generate an inverted phase shift of the nuclei spins, followed by another magnetic field gradient pulse that refocuses the nuclei spins [46, 48]. If the spin does not diffuse during the delay the net phase shift will zero, but if the spin does diffuse during the delay the net phase shift will lead to an attenuation of the observed NMR signal, which is directly related to the value of the diffusion coefficient, according to the Stejskal-Tanner equation [46, 47]

$$A = A_0 \cdot e^{-D\cdot(\gamma\cdot\delta\cdot g)^2\cdot\left(\Delta-\frac{\delta}{3}\right)} \qquad \textbf{Eq. 9}$$

where A and A_0 is the integral of the peak at a gradient g and gradient zero respectively. D is the diffusion coefficient, γ the magnetogyric constant of the nucleus, δ the diffusion gradient pulse length, g the gradient field strength and Δ the diffusion time [49]. The self-diffusion coefficient observed for the surfactant above CMC reflects the population average diffusion of the free unimers and the surfactants aggregated in micelles. This is described by Equation 10, which is based on the assumption that the surfactant can undergo free diffusion in both as unimers and the micelles [50]. As can be seen in Figure 9, the self-diffusion coefficient of the pure micelles can be found by fitting this equation to the observed diffusion coefficients (above the CMC, i.e. in Region 2) plotted against surfactant concentration [50].

$$D_{obs} = D_{uni} \cdot \frac{C_{uni}}{C_1} + D_{mic}\left(1 - \frac{C_{uni}}{C_1}\right) \qquad \textbf{Eq. 10}$$

D_{obs} is the observed diffusion coefficients, C_1 the surfactant concentration, C_{uni} the concentration of the free unimers, D_{uni} and D_{mic} are the diffusion coefficients of the free unimers and micellized surfactants, respectively. With unobstructed diffusion the self-diffusion coefficient of the micelles can be used to calculate the radius of the micelles from the Stokes-Einstein equation

$$D = \frac{K_B \cdot T}{6 \cdot \pi \cdot \eta \cdot r} \qquad \textbf{Eq. 11}$$

where K_B is Boltzmann's constant, T the absolute temperature, η the dynamic viscosity, r the radius, and D the diffusion coefficient [51].

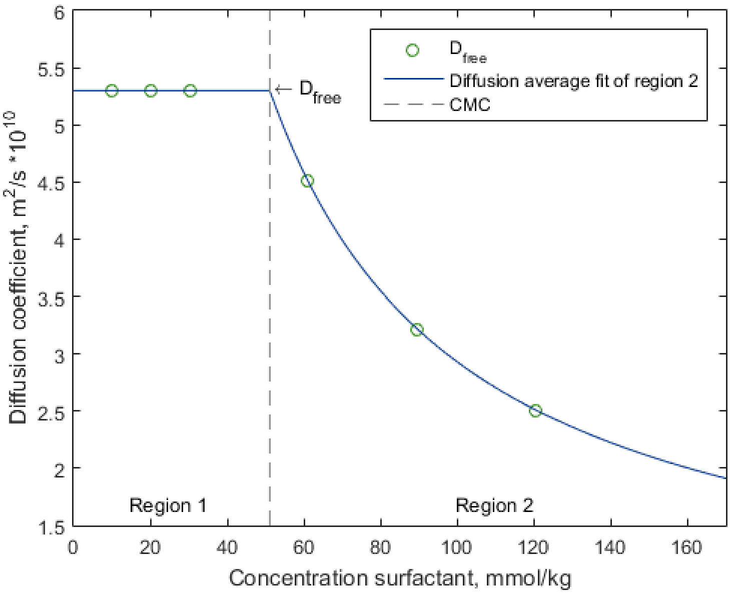

FIGURE 9. FITTING OF THE DIFFUSION AVERAGE EQUATION (EQ. 10) TO THE OBSERVED DIFFUSION COEFFICIENTS IN THE REGION ABOVE CMC (REGION 2).

2.3.4.3. NOESY

NOESY is a homonuclear two-dimensional NOE (Nuclear Overhauser effect) spectroscopy method for determining the relative orientations of atoms in a molecule, or the relative positions of molecules in solution [52, 53]. According to Claridge [52] "The NOE may be defined as the change in intensity of one resonance when the spin transitions of another are somehow perturbed from their equilibrium populations", where the perturbation is caused by radio frequency saturation of one spin at a time. The NOE is derived from through-space magnetic interaction of nuclear spins through dipolar couplings [52]. Crosspeaks in NOESY are caused by incoherent transfer of magnetization between spins during the mixing time, which makes mapping of through-space proximities possible over distances <5 Å [52, 54]. Thus a crosspeak in NOESY represents NOE interactions between two nuclei due to closeness in space and not through chemical bonds, and the sign of the crosspeaks give information about the dynamics of the interaction [52]. This method can be used to detect interactions between different chemical species in solution, for example between a surfactant tail and an oil in a micro-emulsion, to gain information about if the two species are situated close to each other in the observed system.

3. EXPERIMENTAL PROCEDURE

In the following paragraphs the experimental procedures of this project are briefly described. The chemicals used in this project include five surfactants;

- S1, a short chained anionic surfactant
- S2, a non-ionic surfactant with a broad size distribution range
- S3, a non-ionic surfactant with a narrow size distribution range
- S4, a short chained sugar-based biodegradable non-ionic surfactant
- S5, another short chained sugar-based biodegradable non-ionic surfactant

and two additives;

- A1, a weakly basic pH-regulating (short) water-soluble organic molecule
- A2, a strong basic organic molecule with similar functional groups as A1

together with one organic solvent (an aromatic alcohol), and deionized purified water (resistivity 18.2 MΩ/cm). The cold stripping product provided by EnviroStripp consists of S1, A1 (added to help with the long-time stability of the product) and the organic solvent, along with an additional additive that has been excluded from the formulation during this project since it does not have a crucial role in the paint stripping process. For all the sample preparations during the project the components were weighed and added to vials in the order; surfactant, additive, water, solvent.

3.1. TERNARY PHASE DIAGRAMS

The samples (10 g) were prepared gravimetrically and mixed with a vortex mixer to see if they turned turbid or if they were one phase systems, after which dots representing this composition, in weight percent, were plotted in the ternary phase diagram. A number of ternary plots were made where the weight percent additive was varied, and with substituting part of the surfactant with a non-ionic surfactant. The samples were also both heated, up to 70 °C, and cooled to 4 °C to make phase diagrams at different temperatures. According to previously studies by Andersson [14] the stripping efficiency of the system is highest close to the phase separation border, and therefore the study is focused in this area.

3.1.1. PAINT STRIPPING TEST

The paint stripping efficiency was tested according to a standard method developed by Andersson [14], at room temperature. For each sample, two puddles of ten droplets each were applied to the painted surface of a tile strip[1]. The puddles were covered with a watch glass to avoid evaporation, and a stopwatch was used to determine the required time for each puddle to strip the paint. A completed stripping process was indicated by wrinkles and roughness emerging in the paint all over the area covered by the puddle, see Figure 10. The average time required to complete the stripping process for each sample, in the phase diagram, was calculated.

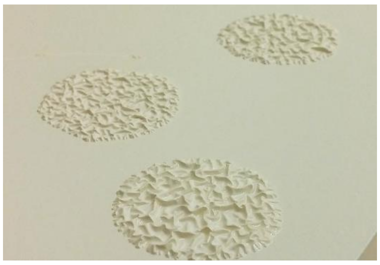

FIGURE 10. PAINT STRIPPING CAUSED BY THE APPLICATION OF CHEMICAL PAINT STRIPPER TO THE SURFACE OF A PAINTED TILE STRIP.

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[1] Beijer bygg art nr: 868901611024 according to standard procedure by Andersson

3.2. SURFACE TENSION MEASUREMENTS

The surface tension was measured using the du Noüy ring method to determine the CMC of different compositions (Platinum ring, minimum of 20 measurements or 300 seconds analysis time per sample to find a mean value). To determine each CMC twelve samples with the same composition regarding additive and solvent, but with varying amount of surfactant, were prepared by weight and then measured in beakers cleaned with Deconex, ethanol and distilled water. Before every measurement the du Noüy ring was burned with a Bunsen burner to get rid of impurities. The surface tension was then plotted against the amount of surfactant, to get the CMC of the system. In addition both the Gibbs and Langmuir equations, Equation 4 and 6 respectively, were fitted to the data to get the surface coverage of surfactants.

3.3. CONDUCTIVITY MEASUREMENTS

Conductivity measurement were done to find the degree of ionization and to confirm the rough estimations of CMC from tensiometry measurements. Continuous conductivity measurements were then done by titration, i.e. repeated addition of a fixed volume (calculated to get a total of 30-40 measured points over the desired surfactant concentration range) to the concentrated sample, on the systems with ionic surfactant and the conductivity was plotted against the amount of surfactant. The titration measurements were compared with point by point measurements (on S1 in water) to validate that the dynamic of the system was fast enough to give the same result in both experiments.

3.4. NMR SPECTROSCOPY

A Bruker Avance 600 spectrometer was used to record both the one-dimensional ^{1}H NMR spectra, and the PGSE diffusion experiments. The self-diffusion coefficients were then plotted against surfactant amount, and this data was fitted with Equation 10 to find the diffusion coefficient of the micelles after which this coefficient was used to determine the size of the micelles in each system with Equation 11. The chemical shifts of the surfactant in the ^{1}H NMR spectra were plotted against the surfactant concentration to verify the CMC determined by conductivity.

For the NOESY spectra a Varian MR 400 spectrometer was used with an internal lock solvent of D_2O (consisting of replacing 20 wt% of the water with D_2O).

3.5. PH ANALYSIS

The pH was measured with a Metrohm Primatrode™ combination electrode and an 827 pH lab meter from Metrohm.

4. RESULTS AND DISCUSSION

The experimental results from this project will be presented and discussed in the following sections, starting with a presentation of the phase diagrams, followed by paint stripping tests, a discussion on the different models and fittings used during the project, a determination of CMCs, a survey of micellar properties based on a compilation of experimental results, and a discussion of the different components influence on the system.

4.1. PHASE DIAGRAMS

The phase diagram made by varying the composition of S1, solvent and water around EnviroStripp's product composition (6 wt% S1 and 18.8 wt% solvent, marked with a star) can be seen in Figure 11. It corresponds well to previous work by Andersson [14], with the difference in presented percentage composition of each point originating in the different assignations of A1 as a co-surfactant (as assigned by Andersson) or not (as assigned in this project). In this project A1 is not viewed as a co-surfactant but rather as a polar co-solvent, and thus included on the water-axis in the phase diagram.

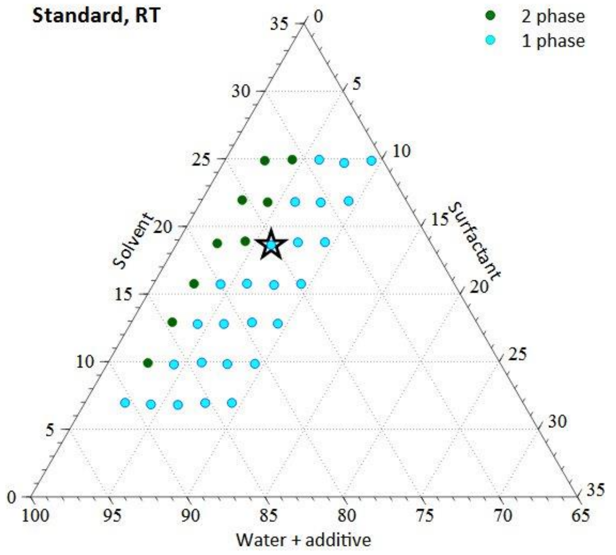

FIGURE 11. PHASE DIAGRAM OF COMPOSITIONS AROUND ENVIROSTRIPP'S PRODUCT (MARKED WITH A STAR) CONTAINING; S1, A1, SOLVENT AND WATER. WHERE THE RATIO OF S1 TO A1 IS KEPT CONSTANT.

Lowering the amount of A1 in the sample compositions to half, compared to the standard phase diagram, changes the sample with 6 wt% S1 and 24.8% solvent along with the 4.3 wt% S1 and 15.8 wt% solvent sample from a one phase system to a two-phase system, as seen in Figure 12. Whereas removing the A1 completely also changes the 6 wt% S1 and 21.8 wt% solvent to a two-phase system, see Figure 13, which indicates that A1 shifts the phase border to a slightly higher position i.e. more solvent can be dispersed in the system when A1 is present.

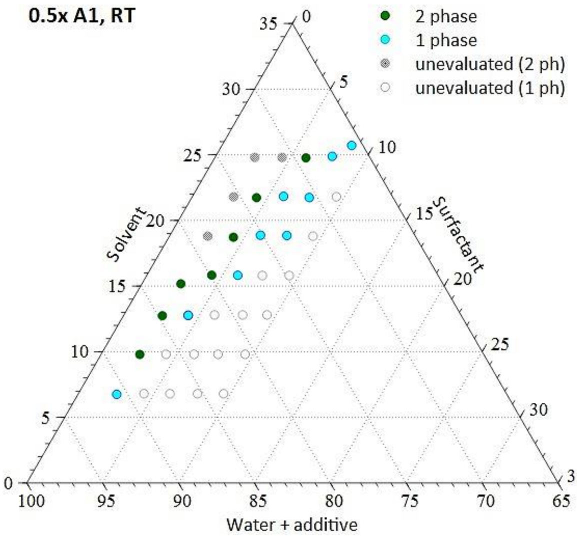

FIGURE 12. PHASE DIAGRAM WHERE THE AMOUNT OF A1 IS HALVED COMPARED TO THE *STANDARD, RT* PHASE DIAGRAM.

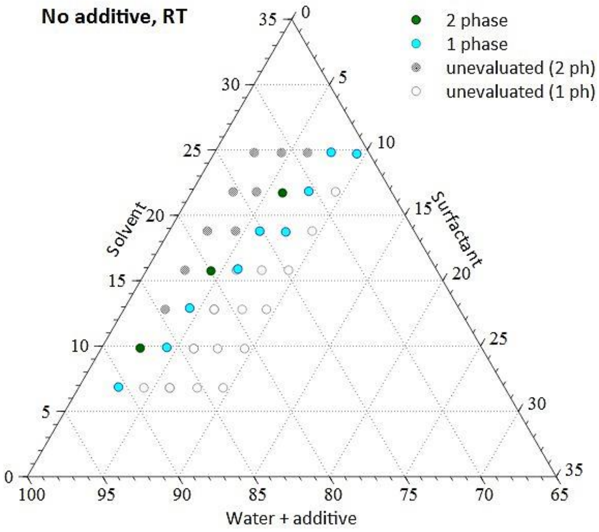

FIGURE 13. PHASE DIAGRAM WHERE A1 HAS BEEN REMOVED COMPARED TO THE *STANDARD, RT* PHASE DIAGRAM.

Replacing A1 with A2 raises the phase border (i.e. shifts the border towards including higher solvent concentrations without phase separating), see Figure 14, which may be an unwanted change when the goal is to improve the studied commercial product (EnviroStripp's composition) since Andersson [14] reported that the stripping efficiency was best close to the phase border. Therefore substituting A2 for A1 may lead to a decrease in stripping efficacy at the studied compositions. Since the desired improvements include lowering the amount of surfactant and/or solvent in the formulation, a lowering of the phase border should be favourable.

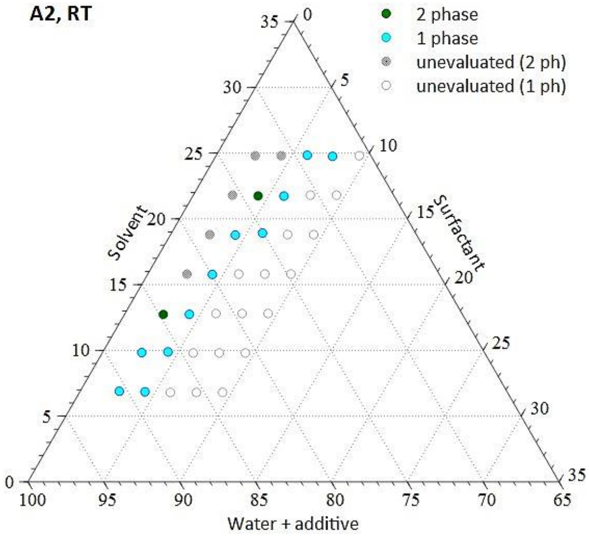

FIGURE 14. PHASE DIAGRAM WHERE A1 HAS BEEN REPLACED BY A2 (WITH RESPECT TO AMOUNT OF SUBSTANCE, AND WHERE WATER WAS REMOVED TO KEEP THE CONCENTRATIONS CONSTANT) COMPARED TO THE *STANDARD, RT* PHASE DIAGRAM.

While making the phase diagrams with 20 wt% substitution of S1 to S2, and S3 respectively the samples precipitated and formed other inhomogeneities, which were not deemed suitable for the continued studies and both S2 and S3 were thus discarded as possible substitutes for S1. Instead S4 and S5 where investigated as potential candidates for partial substitution of S1 and their phase diagrams can be seen in Figure 15 and Figure

16 respectively. Both S4 and S5 displays a lowering of the phase border compared to the standard phase diagram, but the variation is more pronounced for S5 which makes it a stronger candidate for the partial substitution of S1.

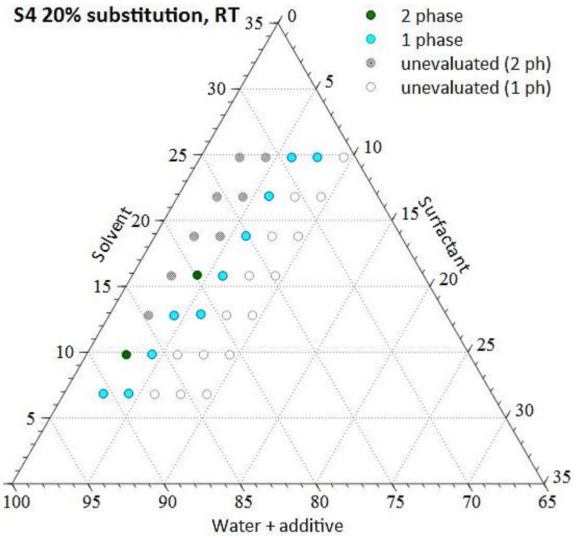

FIGURE 15. PHASE DIAGRAM WHERE 20 WT% OF S1 HAS BEEN REPLACED BY S4 COMPARED TO THE *STANDARD, RT* PHASE DIAGRAM.

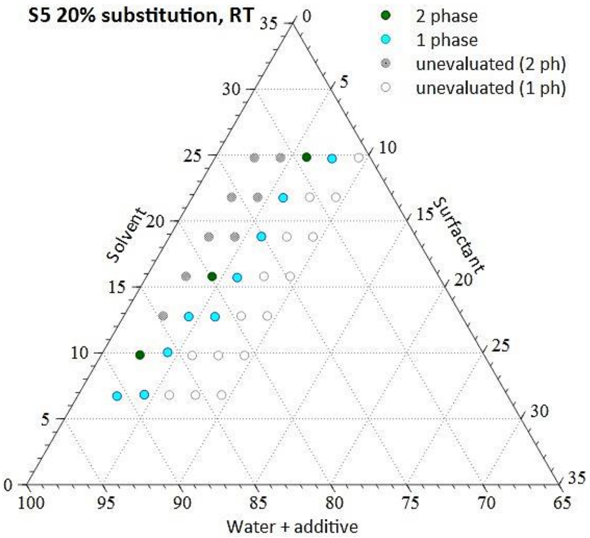

FIGURE 16. PHASE DIAGRAM WHERE 20 WT% OF S1 HAS BEEN REPLACED BY S5 COMPARED TO THE *STANDARD, RT* PHASE DIAGRAM.

The standard phase diagram was also investigated at different temperatures and the new conditions only shifted the phase border slightly (see Appendix I). In conclusion the observed system does not seem very prone to change upon changed conditions, neither when exposed to a wide temperature range, nor upon substitution of different components. This indicates that the system is quite robust, which is advantageous since the product should be used over a long period of time, where slight changes in both composition (due to for example evaporation and mixing in large quantities which lowers the precision) and process temperature are likely to occur.

4.2. PAINT STRIPPING

The results from the paint stripping tests are compiled in Table 1-6 and the different colours represents the efficacy of the composition according to a green to red gradient from 4 minutes and 30 seconds to 20 minutes. The stripping tests with samples from the standard phase diagram, see Table 1, exhibit a trend that corresponds well with previous stripping tests done by Andersson on the same system [14]. The overall slightly faster stripping times achieved in this project were probably due to the systematic user error when determining when the stripping process had been completed, combined with a slightly different set-up with only ten droplets in each puddle instead of twenty.

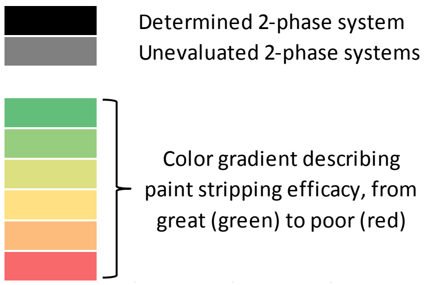
Determined 2-phase system
Unevaluated 2-phase systems
Color gradient describing paint stripping efficacy, from great (green) to poor (red)

FIGURE 17. COLOUR CODE EXPLANATION FOR THE PAINT STRIPPING TESTS PRESENTED IN TABLE 1-6.

Table 1. Stripping test with samples from *Standard, RT* phase diagram, where the wt% of S1 ranges from 2.6 to 9.4 (from the left column to the right) and the wt% of solvent for each row is shown on the left. EnviroStripp's product composition is found at 6.0 wt% surfactant and 18.8 wt% solvent, marked with bold text.

	2.6	4.3	6.0	7.7	9.4
24.8	■	■			
21.8	■	■	06:26		
18.8	■	■	**06:25**		
15.8	■	08:10	09:48		
12.8	■				
9.8	■				
6.8					

Partial or complete removal of A1 inhibits the stripping somewhat compared to the standard (see Appendix I for the complete standard phase diagram, in the studied area, by Andersson [14]) and gives a slower stripping, as can be seen in Table 2 and Table 3. Since A1 is alkaline, and bases often can be used as paint strippers, the decreased paint stripping efficacy when A1 is removed may be caused by the lowered pH of the solution. Therefore decreasing the amount of A1 is probably not the way to improve the stripping efficacy, and seeing as A1 also helps with the long term stability of the product removing it could lead to a shorter life span of the product.

Table 2. Stripping test with samples *from 0.5x A1, RT* phase diagram, where the wt% of S1 ranges from 2.6 to 9.4 (from the left column to the right) and the wt% of solvent for each row is shown on the left.

	2.6	4.3	6.0	7.7	9.4
24.8	▨	▨	■	07:22	06:57
21.8	▨	▨	07:00	07:24	
18.8	▨	▨	08:10		
15.8	■	■	10:04		
12.8	■	08:22			
9.8	■				
6.8	20:00				

Table 3. Stripping test with samples from *No additive, RT* phase diagram, where the wt% of S1 ranges from 2.6 to 9.4 (from the left column to the right) and the wt% of solvent for each row is shown on the left.

	2.6	4.3	6.0	7.7	9.4
24.8	▨	▨	▨	05:31	07:44
21.8	▨	▨	■	07:16	
18.8	▨	▨	07:41	08:55	
15.8	▨	■	10:02		
12.8	▨	08:39			
9.8	■	20:00			
6.8	20:00				

Table 4 shows the effect of replacing A1 with equal amount of substance of A2, which gives an overall inferior stripping efficacy except for the composition 4.3 wt% S1 and 18.8 wt% solvent. At this composition, the stripping efficiency is comparable to those of the samples in the standard phase diagram. However, since this composition is a two-phase system in the standard phase diagram, a comparison of the paint stripping efficiency for this particular composition is not possible. Additionally the efficacy of the systems with A2 decreases rapidly with changes in composition of solvent and surfactant, which could pose a problem if the concentrations change even slightly. Ideally the product should be used over a long time, where changes in concentrations are likely to occur due to factors such as evaporation and refills of water. Thus it can be determined that A2 can achieve a similar paint stripping efficacy as the standard formulation at one specific composition (4.3 wt% S1, 18.8 wt% solvent), but the system with A2 is much less robust than the standard system.

TABLE 4. STRIPPING TEST WITH SAMPLES FROM *A2, RT* PHASE DIAGRAM, WHERE THE WT% OF S1 RANGES FROM 2.6 TO 9.4 (FROM THE LEFT COLUMN TO THE RIGHT) AND THE WT% OF SOLVENT FOR EACH ROW IS SHOWN ON THE LEFT.

	2.6	4.3	6.0	7.7	9.4
24.8	▨	▨	11:23	15:10	
21.8	▨	■	11:30		
18.8	▨	06:57	13:28		
15.8	▨	09:34			
12.8	■	20:00			
9.8	13:41				
6.8	20:00				

A substitution of 20 wt% S1 to S4 or S5 results in paint stripping efficacies similar to that of the standard system, see Table 5 and Table 6. At the composition equivalent to that of studied commercial product (6.0 wt% surfactant, 18.8 wt% solvent) the observed stripping times are almost identical; 6 minutes and 25 seconds for studied commercial product, compared to 6 minutes and 30/38 seconds for S4 and S5 respectively. The partial substitution of S1 for S4 or S5 creates a system that has quite similar phase borders as the standard system, while at the same time displaying a comparable stripping efficacy, which makes S4 and S5 promising candidates that should be studied further. Although the ideal composition with regards to stripping efficacy and surfactant:solvent:water-ratio seems to remain at 6.0 wt% surfactant and 18.8 wt% solvent (as in EnviroStripp's product), the introduction of S4 or S5 lowers the total use of S1, while replacing it with a biodegradable surfactant, which is favourable from an environmental perspective.

TABLE 5. STRIPPING TEST WITH SAMPLES FROM *S4 20 % SUBSTITUTION, RT* PHASE DIAGRAM, WHERE THE WT% OF S1 RANGES FROM 2.6 TO 9.4 (FROM THE LEFT COLUMN TO THE RIGHT) AND THE WT% OF SOLVENT FOR EACH ROW IS SHOWN ON THE LEFT.

	2.6	4.3	6.0	7.7	9.4
24.8	▨	▨	04:50	05:59	
21.8	▨	▨	06:25		
18.8	▨	▨	06:30		
15.8	▨	■	09:05		
12.8	▨	09:16	16:05		
9.8	■	20:00			
6.8	20:00	20:00			

TABLE 6. STRIPPING TEST WITH SAMPLES *FROM S5 20 % SUBSTITUTION, RT* PHASE DIAGRAM, WHERE THE WT% OF S1 RANGES FROM 2.6 TO 9.4 (FROM THE LEFT COLUMN TO THE RIGHT) AND THE WT% OF SOLVENT FOR EACH ROW IS SHOWN ON THE LEFT.

	2.6	4.3	6.0	7.7	9.4
24.8	▨	▨	■	05:36	
21.8	▨	▨	05:51		
18.8	▨	▨	06:38		
15.8	▨	■	10:29		
12.8	▨	07:08	17:01		
9.8	■	13:30			
6.8	20:00	20:00			

It should be noted that partial substitution of S1 for S4 and S5 seems to cause a different trend in efficiency along the phase border of the system, compared to the complete standard system observed by Andersson [14]. The partially substituted systems display a diagonal trend along the phase border from higher to lower concentrations, where the efficacy decreases with decreasing concentrations of both solvent and surfactant, whereas Andersson observed a trend of lowered efficacy foremost along the other diagonal – from closest to the phase border to the compositions furthest away from it. Thus, a more thorough investigation of the stripping efficacy of the complete phase diagrams with both 20 wt% S4 and S5, together with the standard phase diagram, should be carried out to get a more uniform and detailed view of the systems.

4.3. PHYSICOCHEMICAL STUDIES OF THE BULK PROPERTIES

In the following sections, the bulk properties of the system will be analysed and discussed based on the results from the physicochemical studies, starting with a determination of the CMCs, followed by an investigation of the micellar properties, and then a discussion on the different components influence on the system. Due to multiple interactions between the components at high concentration, the physicochemical studies of the bulk properties are done at considerably lower concentrations than the phase diagram and paint stripping tests.

4.3.1. DETERMINATION OF CMC

Surface tension and conductivity measurements were used to study the CMC of the surfactants in solutions of different composition. Since surface tension analysis requires point-by-point measurements it is a time-consuming method for precise determination of the CMC. Thus this method was used to estimate the CMC, and this estimation was then validated by conductivity measurements, which can be performed by continuous titration over a concentration range. This allows fast and precise determination of the CMC, why this method was deemed most suitable to determine the specific value of the CMC. ^{1}H NMR chemical shifts of the surfactant were studied to validate the obtained CMC values, but since neither an internal nor external reference was present, the uncertainty of the results were too large to give any reliable results, and were thus discarded.

Fitting of conductivity data was made by assuming a linear trend for the measured values on each side of the studied concentration range, to which two linear functions were fitted, as seen in Figure 18. Visual inspection verified this assumption regarding correspondence with the measurements over the remaining concentration range. The CMC was calculated from the intercept of the two lines.

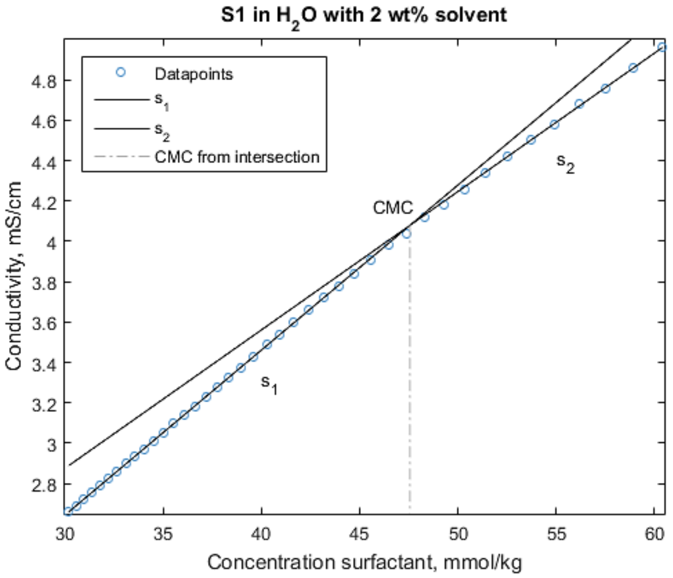

FIGURE 18. FITTING OF LINEAR FUNCTIONS IN EACH END OF THE STUDIED CONCENTRATION RANGE TO CONDUCTIVITY MEASUREMENTS.

Fittings of conductivity data for all the studied systems in this project can be found in Appendix IV. The obtained CMC values from this fitting correspond well to the values of the CMCs determined from surface tension measurements.

The determined CMC of 110 mmol/kg for S1 in water corresponds well to earlier studies by Maham et al. on the same surfactant [55]. As can be seen in Table 7 and Figure 19, addition of solvent decreases the CMC of S1, while increased amount of A1 does not induce any change in the CMC. A1 does however seem to amplify the effect of the solvent when both are present, causing an even greater decrease in the CMC, as seen in Figure 19.

TABLE 7. CMC IS DERIVED FROM CONDUCTIVITY MEASUREMENTS, EXCEPT FOR S4 AND S5 (NON-IONIC SURFACTANTS) FOR WHICH TENSIOMETRY WAS USED TO DETERMINE CMC. ST AT THE PLATEAU IS DETERMINED BY THE DU NOÜY RING METHOD.

System	**Solvent [wt%]**	**Additive [mmol/kg]**	**CMC [mmol/kg]**	**ST at plateau [mN/m]**
S1 in water	-	-	110	39
S4 in water	-	-	Around 100*	-
S5 in water	-	-	Around 60*	29
S1, solvent	1	-	71	36
S1, solvent	2	-	48	35
S1, solvent	3	-	31	34
S1, A1	-	250	98	38
S1, A1	-	500	105	38
S1, A1	-	750	104	37
S1, A1, solvent	1	750	64	-
S1, A1, solvent	2	750	41	35

*hydrotropic behaviour, see Appendix II

As noted by Rosen [20], alcohols that reduce the CMC are adsorbed in the outer parts of the micelle, and thus the distinct decrease in CMC with addition of solvent indicates that the solvent would be included in the palisade layer of the micelle, making a co-surfactant-like behaviour of the solvent plausible. This requires good interactions between S1 and the solvent, which is facilitated when the surfactant and co-surfactant have similar tail lengths and when the co-surfactant has a straight chained tail [20]. Thus the solvent should resemble S1 in size and shape to promote co-surfactant behaviour. An examination of the molecular structure of the solvent supports the suggestion that the solvent is acting as a co-surfactant, since the solvent molecule has properties resembling those of a medium-length aliphatic surfactant even though it contains an aromatic ring [56, 57]. Seeing as S1 is a relatively short surfactant, the similarity in size and properties of S1 and the solvent promotes interaction between the two species. The lack of change in CMC when only A1 is added to the system makes it unlikely that strong interactions are occurring between A1 and S1. Thus A1 is probably not included in the micelles, but instead affecting the properties of the water phase. Commonly used co-solvents are ethanol, glycerol and polyethylene glycol (PEG) [58], which also works by affecting the water properties to increase the solubility of poorly water-soluble molecules.

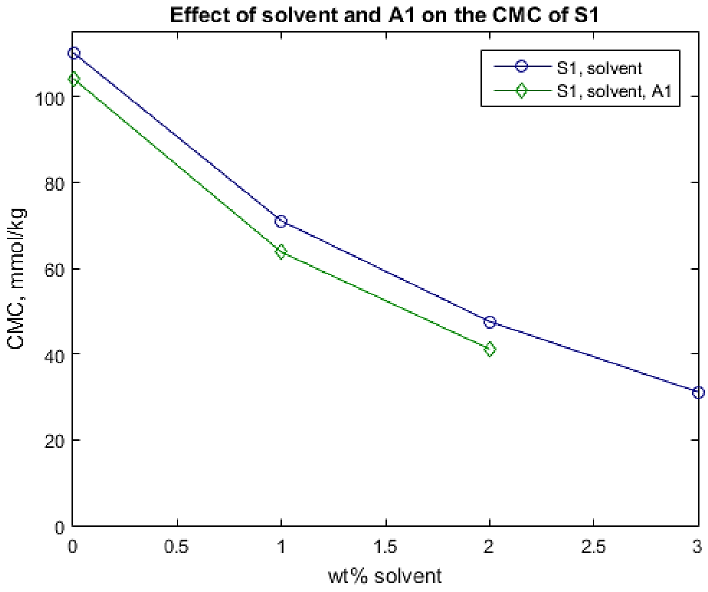

FIGURE 19. EFFECT OF SOLVENT AND A1 ON THE CMC OF S1.

Both S4 and S5 are non-ionic surfactants with hydrotropic behaviour, and as hydrotropes do not have a CMC value, the CMC values listed for S4 and S5 are approximations of when the slope of the surface tension curve has levelled out. Since S4 and S5 are considered as replacements to S1, their physical properties should be similar to those of S1 to be compatible with the system they are introduced to, and not worsen the stripping properties to a significant extent. The CMC of non-ionic surfactants are often much lower than those of ionic surfactants [17], which could give rise to some problems upon substitution into the existing system of ionic surfactants. Thus, the unusually high "CMC" values of S4 and S5 is an indication of their potential to be good substitutions to S1 in studied commercial system without changing the properties of the system considerably.

No major changes in the plateau values of the surface tension above the CMC was found upon addition of solvent, A1 or with partial substitution of S1 for S4 or S5 compared to S1 in water. This indicates that the surface activity of the system does not change to any greater extent when introducing these components.

4.3.2. MICELLAR PROPERTIES

To investigate the micellar properties the size of the micelles was studied using PGSE NMR spectroscopy, information on the surface area per surfactant head group in the micelles was derived from surface tension measurements, and the degree of ionization was studied using conductometry by analysing the two slopes from conductometry (see s_1 and s_2 in Figure 18). The mole fraction of solvent in the micelles was then studied using calculations based on the CMCs of the systems.

The obtained self-diffusion coefficients of the surfactant from PGSE NMR spectroscopy were fitted using the diffusion average equation (Eq. 10), where the measured diffusion coefficients above the CMC corresponds well with the model assumptions, see Figure 20. Additional diffusion fitting plots for all the studied systems can be found in Appendix V.

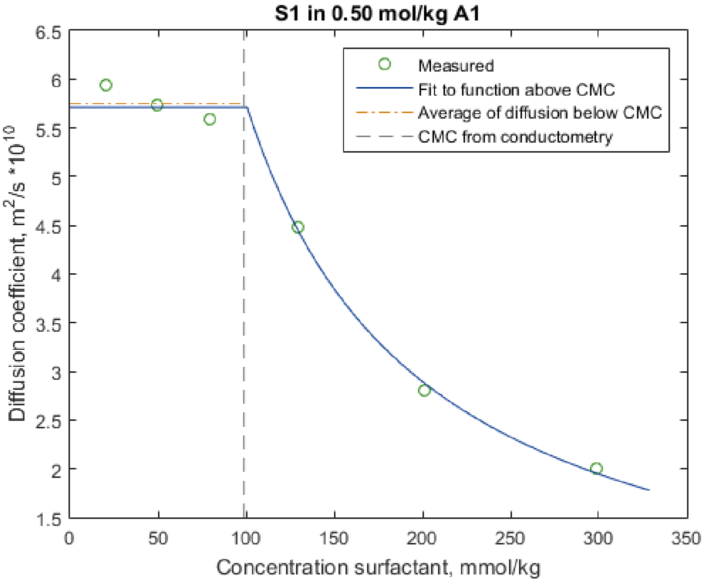

FIGURE 20. FITTING OF THE DIFFUSION AVERAGE EQUATION TO THE DIFFUSION MEASUREMENTS AT DIFFERENT SURFACTANT CONCENTRATIONS.

Ideally, the diffusion rate of the monomers should be constant below the CMC, but as can be seen in Figure 20 the observed diffusion coefficients in this project display a decrease in diffusion coefficient of the surfactant with increased surfactant concentration even below the CMC. This effect could be caused by an increased viscosity of the liquid phase with addition of surfactant since the pure surfactant has a larger viscosity than water, but seeing as S1 is a relatively short surfactant molecule, a viscosity increase of the observed magnitude is not likely to originate solely in the increased amount of unimers. Another explanation could be that S1 forms dimers and trimers in solution below the CMC, which would also cause a decrease in average diffusion rate of the monomers since these small aggregates will have a slower diffusion rate due to their size.

The diffusion average equation (Eq. 10) is a simplified model that does not take into account various effects from obstruction and electrostatic interactions between the micelles. Thus the radii calculated from this equation must be interpreted with care, and the possibility of unaccounted effects in the system must be considered.

To acquire information on the surface area of the surfactant head groups in the micelle the Gibbs and Langmuir equations (Equation 4-6) were used to fit the surface tension data. Both equations are fitted to the measured surface tensions below the CMC of the system plotted against the logarithm of the concentration of surfactant, but the Gibbs equation should be fitted to the final slope of this region as it approaches CMC, as can be seen in Figure 21, while the Langmuir equation is fitted to all recorded values below the CMC, as seen in Figure 22.

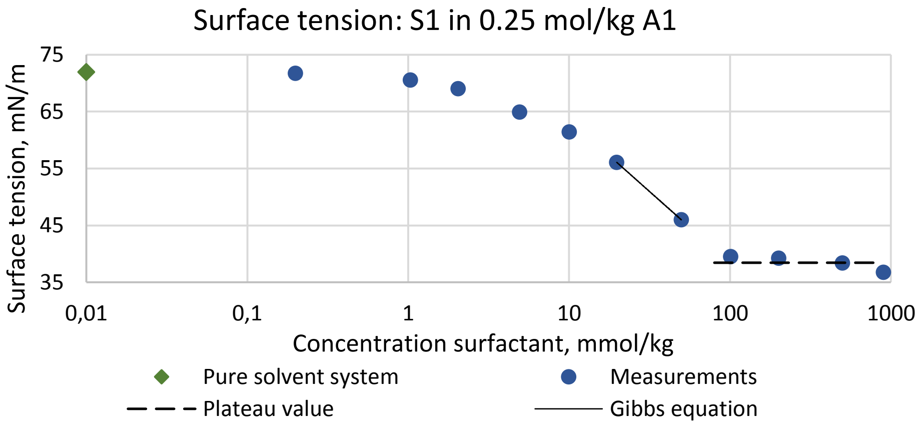

FIGURE 21. FITTING OF SURFACE TENSION MEASUREMENTS (POINTS IMMEDIATELY BELOW THE CMC) WITH THE GIBBS EQUATION.

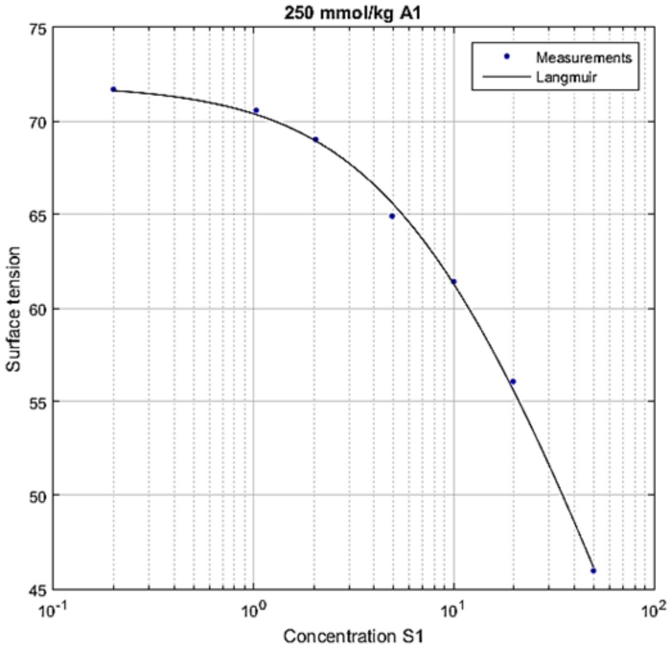

FIGURE 22. FITTING OF ALL SURFACE TENSION MEASUREMENTS BELOW THE CMC WITH THE LANGMUIR EQUATION.

Plots displaying all Gibbs and Langmuir fittings of all the systems analysed in this project can be found in Appendix II and III. The Langmuir fitting appears to be in good agreement with the trends in measured data, but since the measured points in the regions close to the CMC are widely spaced, the Gibbs equation fitting was not always optimal. However the calculated surface areas from both fittings show an overall good agreement.

Table 8 presents data on the radius of the micelles calculated from PGSE NMR spectroscopy data (Equation 9-11) where the increase in viscosity of the solution when A1 is present has been accounted for [59], the surface area of the surfactant head groups in the micelle derived through Gibbs and Langmuir fittings of surface tension measurements (Equation 4-6), and the degree of ionization determined from conductivity measurements (Equation 7).

TABLE 8. RADIUS OF MICELLES DETERMINED FROM FITTING OF PGSE NMR SPECTROSCOPY DATA (EQUATION 9-11), DEGREE OF IONIZATION FROM CONDUCTIVITY MEASUREMENTS, AND a_0 DETERMINED FROM BOTH GIBBS AND LANGMUIR FITTINGS.

System	**Solvent [wt%]**	**Additive [mmol/kg]**	**Radius [nm]**	**Degree of ionization**	**a_0, Gibbs [Å^2]**	**a_0, Langmuir [Å^2]**
S1 in water	-	-	10.5	0.69	78	68
S1, solvent	1	-	3.27	0.80	119	128
S1, solvent	2	-	2.34	0.84	148	163
S1, solvent	3	-	1.28	0.92	145	163
S1, A1	-	250	38.79	0.93	75	73
S1, A1	-	500	46.22	0.83	82	-
S1, A1	-	750	-	0.75	92	76
S1,A1, solvent	1	750	-	0.93	-	-
S1, A1, solvent	2	750	1.95	0.92	186	220
S1:S5 (4:1), A1, solvent	2	750	1.64	-	-	-

It should be noted that the observed degree of ionization for S1 in water is significantly higher than earlier studies suggest, where it was found to be 0.58 [55]. Based on the length of the hydrophobic tail (estimated according to Rosen [19]), it can be derived that if S1 forms spherical micelles, they cannot have a diameter larger than 2.58 nm [18], where a diameter of 2.06 nm should be expected since the tail consists of a saturated straight chain. This is much smaller than the radius of 10.5 nm reported in Table 8, which indicates that the micelle is either not shaped like a sphere, or subjected to obstruction effects that lower the observed diffusion coefficient and thus gives a lower calculated diffusion coefficient of the micelle. The suggestion of the micelle having another shape than spherical is supported by the packing parameter for S1 in water. Calculated from a_0 and estimations of l_c and V_H (according to Rosen [19]) with Equation 5 it has a value of 0.33-0.38 (derived from a_0-values of both Gibbs and Langmuir respectively), and a packing parameter of this size lies in between the regions where a spheroidal and a cylindrical shape can be expected [19], thus an elongated shape of the micelles is plausible for the system. With obstruction effects the calculated radius will assume a value higher than the actual size of the micelle since the Stokes-Einstein equation (Equation 11) is based on unobstructed diffusion of the micelle [60]. Obstruction will lower the observed diffusion coefficient, which in turn leads to a lower diffusion of the micelle when calculated with Equation 10, which leads to a larger calculated radius. Since the CMC is rather high for S1 in aqueous solution, it is likely that the high amount of charged unimers, counterions and micelles cause significant electrostatic obstructions.

Upon addition of solvent the micelle radius decreases, while the surface area per molecule increases. The radii presented in Table 8 for systems containing S1 and solvent are well in line with expected sizes of aggregates in microemulsions (the reported radii are even quite small compared to other microemulsions), as well as in good accordance with the aforementioned calculated radius of 2.06 nm based on the structure of S1. Since the solvent lowers the CMC significantly, the obstruction effects should be lower with solvent present compared to S1 in aqueous solution due to the system being more dilute. The calculations of a_0 (Equation 4-6) are done with respect to only S1 in the micelles, and thus the result should be interpreted as a larger distance between S1 head groups in the micelle (see Figure 23 for an illustration of the interpretation of a_0 in absence and presence of a co-surfactant). This is another indication of co-surfactant-like behaviour of the solvent, suggesting that it is included in the palisade layer of the micelles. Since the solvent molecules have no ionic charge, they will separate the charges of the S1 head groups in the micelle by being included in the palisade layer, which also increases the observed head group area of the surfactant. The increased degree of ionization when solvent is present means that an increased amount of counterions exist as free species, which indicates a lower driving force to associate with the micelle surface. This is another observation that could be explained by a co-surfactant behaviour of the solvent, since the lowered driving force of the counterions to associate with the micelles indicate that the charge density of the micellar surface is lowered by the solvent. Since fewer counterions bind to the micelle surface, there will be a lower entropic penalty associated with micelle formation, which can explain the decrease in CMC when solvent is introduced [61]. These observations are also in line with earlier observations of the effect of alcohols on surfactant systems by Zana [29].

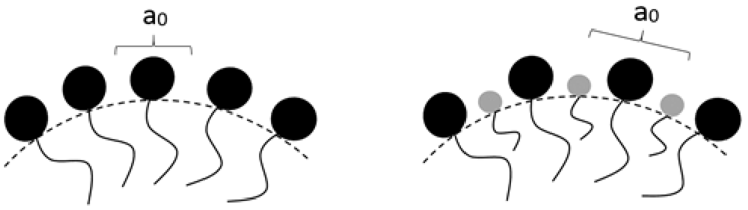

FIGURE 23. SCHEMATIC ILLUSTRATION OF HOW CO-SURFACTANTS (GREY) INCREASE THE CALCULATED SURFACE AREA (a_0) OF THE SURFACTANT HEAD GROUPS.

No clear or consistent trend in the properties listed in Table 8 can be observed with increased concentrations of A1 in the system. In general, an increased degree of ionization and micellar size can be observed compared to S1 in water, while the surface area of S1 is virtually unaffected. The increased degree of ionization without a changed surface area could be explained by the electrolyte properties of A1. With increased electrolyte content in the water phase, the micelle surface charge is less deviant from the surrounding, which leads to a lower driving force of charge neutralization. A1 is too polar to be residing inside the micelles, but may instead act as a co-solvent and change the properties of the water phase when introduced in the system. The increase in micelle size observed when A1 is present are probably caused by the fact that obstruction effects are not accounted for when calculating the diffusion coefficient of the micelle. Since the degree of ionization is high, the repulsion between charged micelles will be strong, and thus cause a large obstructing effect which slows the micelles down and gives a lower value of the diffusion coefficient of the micelle than is true for free diffusion. Additionally A1 has no effect on the CMC, and since the obstruction effects are deemed significant for S1 in aqueous solution due to the high concentration of charged species (see discussion earlier in this section), the same obstructing effects should have an even larger impact in the systems were A1 is present since addition of A1 provides more charged species in the solution.

When A1 is combined with the solvent, it is clear that the effects of the solvent are dominating over those of A1 regarding all properties listed in Table 8. It should also be noted that the surface area of S1 in the micelles increases to a much greater extent when the solvent and A1 are combined, compared to when only solvent is present. Once again, A1 seem to amplify the effect of the solvent.

A 20 wt% substitution of S1 for S5 in the formulation containing 2 wt% solvent and 750 mmol/kg A1 does not seem to have any detrimental effects on the system with respect to the observed properties listed in Table 8, which suggests that S5 may have good compatibility with the studied system.

4.3.2.1. MOLE FRACTION OF SOLVENT IN THE MICELLES

The distribution of solvent in the systems consisting of S1, solvent and water listed in Table 7-8 was calculated with Equation 2 based on the model described by Perez-Villar [32]. This equation is deemed valid for the system studied in this master thesis since it contains an ionic surfactant and an alcohol that self-aggregates in aqueous solution, which is similar to the butanol/SDS-system that the model was developed for [32]. A third degree polynomial was used to describe the variation in CMC with solvent concentration as can be seen in Figure 24. With CMC described as a function of solvent concentration, Equation 2 can be used to create a continuous curve expressing the mole fraction of solvent in the micelles as a function of the mole fraction of solvent in the solution. The report by Perez-Villar et al. contains a more thorough explanation of the fitting procedure [32].

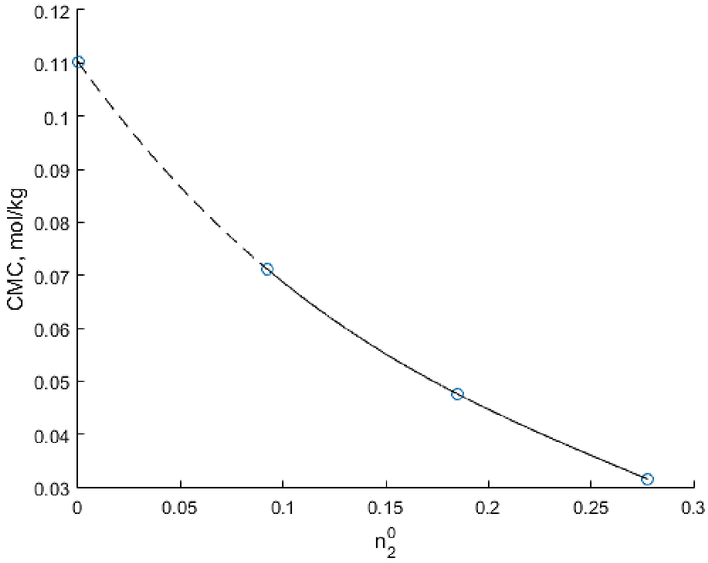

FIGURE 24. FITTING OF A 3^{RD} DEGREE POLYNOMIAL FUNCTION TO THE VALUES OF CMC (DETERMINED WITH CONDUCTOMETRY) PLOTTED AGAINST THE CONCENTRATION OF SOLVENT IN THE SYSTEM (N_2^0, MOL/KG). THE CMC AT 0 MOL/KG SOLVENT WAS INCLUDED TO ENHANCE THE FITTING, BUT THE CALCULATIONS OF MOLE FRACTION IN THE MICELLES IS BASED ONLY ON THE CONTINUOUS FITTED LINE.

Figure 25 show the mole fraction of solvent in the micelles plotted against the mole fraction of solvent in the solution over the studied solvent concentration range. It indicates that the solvent participates to a smaller fraction in the micelles than it does in the solution as a whole, seeing as the plotted line lies below the dashed diagonal marking an equal composition of the micelles as the solution in whole.

Compared to the system studied by Perez-Villar et al. where the distribution in a system containing butanol and SDS is studied, the system containing S1 and solvent has a larger tendency to form mixed micelles containing a substantial proportion of solvent.

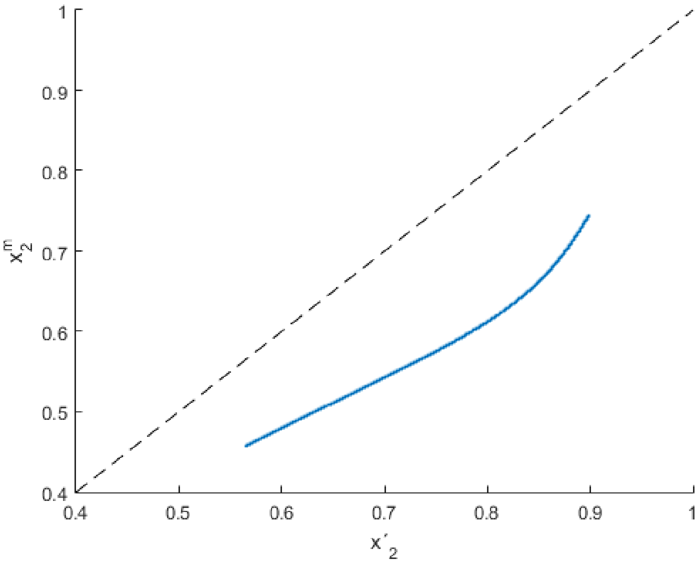

FIGURE 25. MOLE FRACTION OF SOLVENT IN THE MICELLES OF SOLUTIONS CONTAINING S1 AND SOLVENT IN WATER PLOTTED AGAINST MOLE FRACTION OF SOLVENT IN THE SOLUTION.

4.3.3. INFLUENCE OF THE DIFFERENT COMPONENTS ON THE SYSTEM

The effects of the solvent on the observed system properties (CMC, degree of ionization and surfactant head group area) all indicate that the solvent has the function of a co-surfactant. Another observation supporting the suggestion that the solvent is included in the micelles is the similarity of the diffusion behaviour of the solvent and S1 below and above the CMC of the system, as can be seen in Figure 26. The solvent exhibit a similar decrease in diffusion coefficient as the solvent, indicating that they are included in the same part of the system, i.e. the micelles.

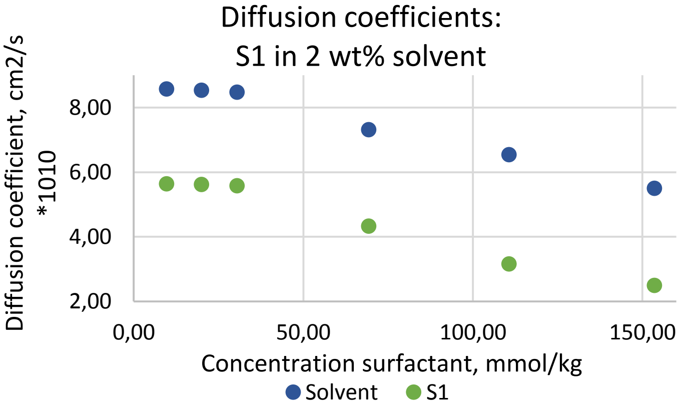

FIGURE 26. OBSERVED DIFFUSION COEFFICIENTS OF SOLVENT AND SURFACTANT IN A SYSTEM OF S1 AND 2 WT% SOLVENT, WHERE THE THREE POINTS FURTHEST TO THE LEFT ARE BELOW THE CMC OF THE SYSTEM.

In review of the paint stripping tests an enhanced stripping is always found when increasing the amount of solvent while maintaining the same concentration of surfactant. Thus it can be deduced that the solvent also has an important effect on the stripping efficacy of the system, although part of the enhanced stripping could be explained by the fact that increased solvent concentration moves the system closer to the phase border, which has been noted before by Andersson [14] to increase the efficacy.

A1 can be viewed as both an electrolyte and a pH-regulator, or even a co-solvent, and as such the effect of this additive is harder to comprehend. Electrolytes does usually have a lowering effect on the CMC [20], which is not observed for this system, but at the same time organic electrolytes are sometimes found to cause an increase in micellar size [30], which A1 seems to do in this system. An investigation of the pH of A1 in aqueous solution show that it creates an alkaline environment with a pH above 11 already at low concentrations, see Table 9. The same alkalinity is also observed in a system consisting of S1, solvent and A1, why addition of A1 is assumed to consistently raise the pH of the observed systems to similar values.

TABLE 9. pH MEASUREMENTS ON DIFFERENT SYSTEMS CONTAINING A1, SOLVENT AND SURFACTANT.

System	**Solvent [wt%]**	**Additive [mmol/kg]**	**S1 [mmol/kg]**	**pH (± 0.1)**
A1 in water	-	25	-	11.11
A1 in water	-	250	-	11.65
A1 in water	-	500	-	11.82
A1 in water	-	750	-	11.95
S1, A1	-	250	100	12.08
S1, A1	-	500	100	12.15
S1, A1	-	750	100	11.98
S1, solvent	1	-	100	9.15
S1, A1, solvent	2	750	100	11.67

Since alkaline substances often have good paint stripping properties [8], the alkaline environment introduced by A1 may contribute to the increased paint stripping efficiency when A1 is present compared to the same system without any additives. The raised pH might also indicate that A1 works as a co-solvent, changing the properties of the water-phase and thus changing the interactions between the phases in the system. Polar solvents other than pure water are usually observed to increase the degree of ionization, and they often raise the CMC of the surfactant if they are strongly polar [17].

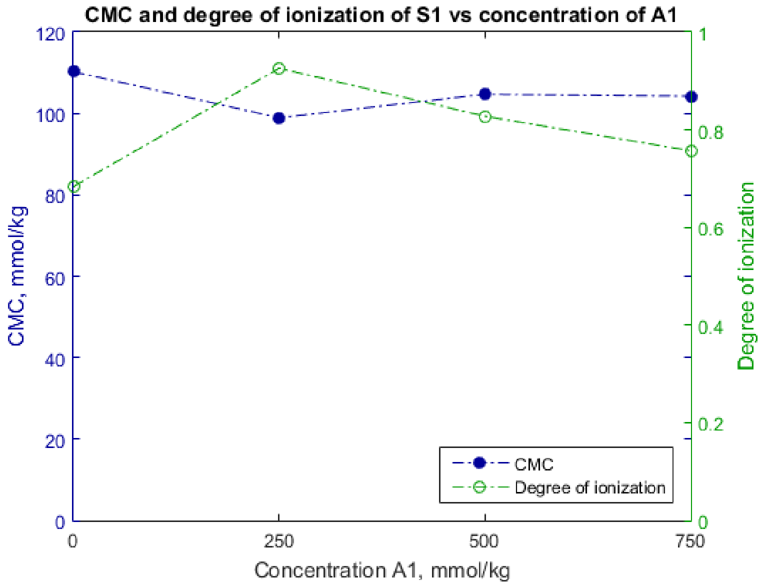

FIGURE 27. CMC VALUES FROM TABLE 7 AND DEGREE OF IONIZATION FROM TABLE 8 PLOTTED AGAINST CONCENTRATION OF A1.

As can be seen in Figure 27 an increase in the degree of ionization is observed when A1 is present, although there appears to be a maximum value around 250 mmol/kg A1. This increase corresponds well to the theory of A1 acting as a co-solvent and changing the bulk properties of the water phase, although there is no clear decrease of the CMC with increased concentration of A1 which contradicts the anticipated effects of a polar solvent. To investigate the co-solvent hypothesis with respect to the solubility of the solvent, a quick study was carried out to compare the solubility of the solvent in water to the solubility of the solvent in a 750 mmol/kg A1 solution. No difference in solubility was detected.

A1 has also been noted to amplify the effects of the solvent on the system when combined, which is illustrated in Figure 28, where the effects of the solvent on CMC and degree of ionization is displayed both in absence of A1 and with a large concentration of A1 present. The decrease in CMC observed upon addition of solvent is even more pronounced in the presence of A1, and the increase in degree of ionization is also amplified by A1. The additional increase in degree of ionization could still be explained by the increased electrolyte content in the solution, as discussed before, but the further decrease in CMC with addition of A1 is harder to explain since A1 does not have any consistent effect on the CMC by itself.

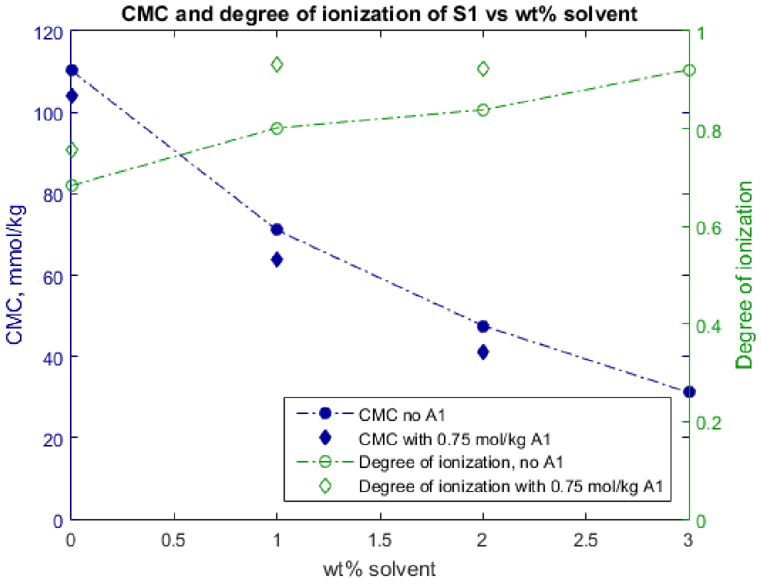

FIGURE 28. CMC VALUES FROM TABLE 7 AND DEGREE OF IONIZATION FROM TABLE 8 PLOTTED AGAINST WT% OF SOLVENT.

The system has been observed to have properties pointing towards a microemulsion structure of the bulk. One of the qualities often mentioned when comparing macro- and microemulsions is the visual appearance of the bulk, where emulsions are turbid while microemulsions are transparent due to the droplets being too small to interact with visible light [62]. Upon inspection of the samples in the phase diagram, all one-phase samples are completely transparent. Microemulsions are also thermodynamically stable while macroemulsions eventually phase separate [21], and no phase separation has been observed in any of the one-phase samples over the course of 20 weeks. On the other hand macroemulsions can be seemingly stable for time periods much longer than this without phase separating [15]. Microemulsions should also form spontaneously with just a slight shaking or mixture required [63], and the prepared samples were found to only require a few seconds of stirring with a vortex or shaking to create the clear one-phase system. Microemulsions are also characterized by having droplets in the a size range around 10 nm or below, and while the calculated dimensions of the micelles in Table 8 indicate that many of the aggregates, especially when the solvent is present, are within this size range, these values are too roughly estimated to make conclusions from, seeing as obstruction and other effects are not accounted for in the calculations.

A few studies with NOESY was carried out on some systems containing solvent, S1, A1 and A2 in different compositions to further investigate the interactions between these components. No conclusions could be drawn from these brief experiments, why further studies with enhanced analysis settings are required.

5. CONCLUSIONS

The aim of this master thesis was to study a chemical paint stripping product to investigate the bulk properties of the formulation. The work was directed towards answering the questions of whether the system consists of a microemulsion, and how each species affect the properties of the system. The possibilities of substituting or decreasing the amount of surfactant and/or additive in the formulation were also examined to try to make the product more environmentally friendly. To answer these questions, a comprehensive study of the paint stripping system has been carried out, using NMR spectroscopy, tensiometry, conductometry, paint stripping tests and phase diagram construction. The same techniques were also used to study systems with altered composition, where the surfactant was partially substituted, with replacement of the additive, or with reduction of the amount of additive in the formulation.

The analyses of the studied paint stripping formulation indicates that it forms a microemulsion. The phase diagram is found to be rather robust, displaying only minor changes in appearance upon variation of the temperature, removal of A1, substitution of A1 for A2, and partial substitution of S1 for S4 and S5. Partial substitution of S1 for S2 or S3 introduced precipitation and other inhomogenities, and thus S2 and S3 were not deemed suitable for further studies. The paint stripping efficacy was found to deteriorate if the concentration of A1 is decrease or if A1 is removed completely from the formulation, and also if A1 is substituted for A2. A 20 wt% substitution of S1 for S4 and S5 gave similar paint stripping abilities as the original product composition, which indicates that they could be good candidates to make the product more environmentally friendly. Physico-chemical studies show that the solvent is acting as a co-surfactant, where it lowers the CMC of S1, increases the degree of ionization of the micelles, increases the surface area per surfactant head group in the micelles, and reduces the size of the micelles. A1 is found to have no significant effect on the CMC or the degree of ionization, but seem to increase the size of the S1 micelles compared to S1 in water. A1 also raise the pH of the systems to a high alkalinity, which may explain the enhanced stripping efficacy observed when A1 is present. The results also indicate that the additive amplifies the effects of the solvent on the system, such as further decreasing the CMC and increasing the degree of ionization.

The solvent in the formulation has previously been regarded as the dispersed phase in the paint stripping microemulsion, but the presented results indicate a more diverse role of the solvent in the system, where it also acts as a co-surfactant. This behaviour of the solvent could provide new insights into the paint stripping mechanism of microemulsions. Another interesting observation is the possibility of partially substituting S1 for the sugar-based biodegradable surfactants S4 or S5 with maintained paint stripping efficacy, since it opens up a potential way to make the formulation more environmentally friendly. Environmental aspects are always important to consider within the paint (stripping) industry since stricter regulations regarding environmental impacts of the businesses are constantly being introduced.

6. FUTURE WORK

To further clarify the role of A1 in the system, it would be interesting to study where it is located in the system and how it interacts with the other components. This could be investigated by for example NOESY.

It would also be interesting to further examine the effect of introducing S4 and S5 as partial substitutes to S1 on the physicochemical properties of the system, such as CMC. The paint stripping efficacy should also be tested on other types of paint than the one used in the standard paint stripping test on a tile strip, to verify that it works on different paint compositions.

Since this thesis work has clarified the role of the solvent in the system at lower concentrations, a study at higher concentrations of solvent could now be a useful continuation to further explore the properties and mechanisms of the paint stripping system at concentrations similar to the one in the commercial product.

7. ACKNOWLEDGEMENTS

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Hanna Andersson and Sara Carlsson, Gothenburg, September 2015

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APPENDIX

I. TERNARY PHASE DIAGRAMS

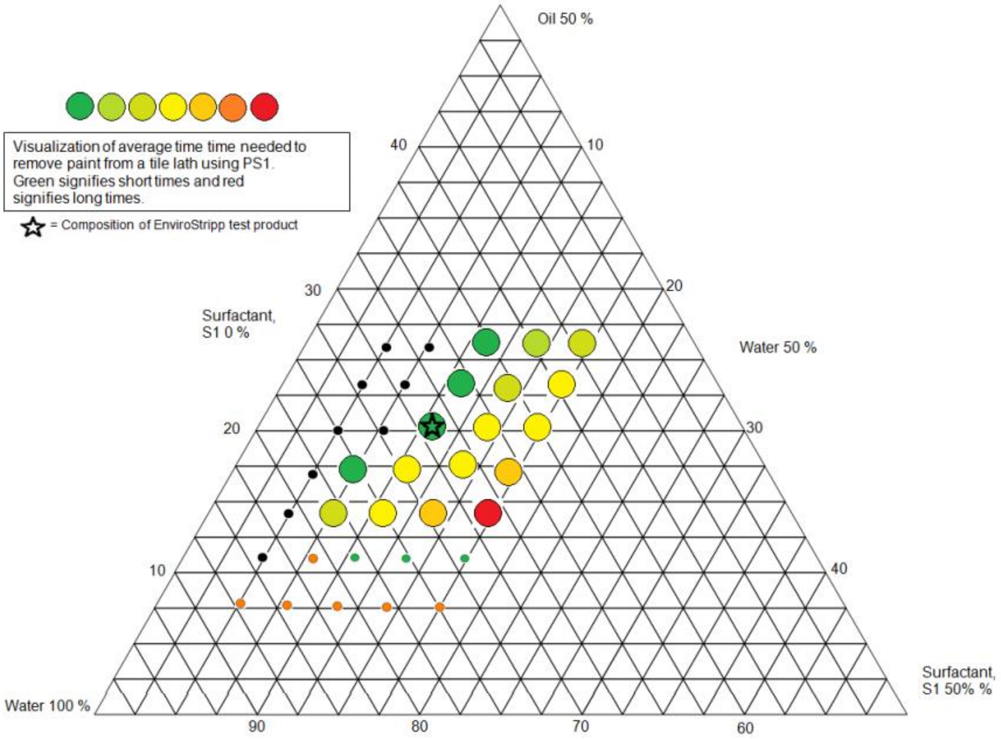
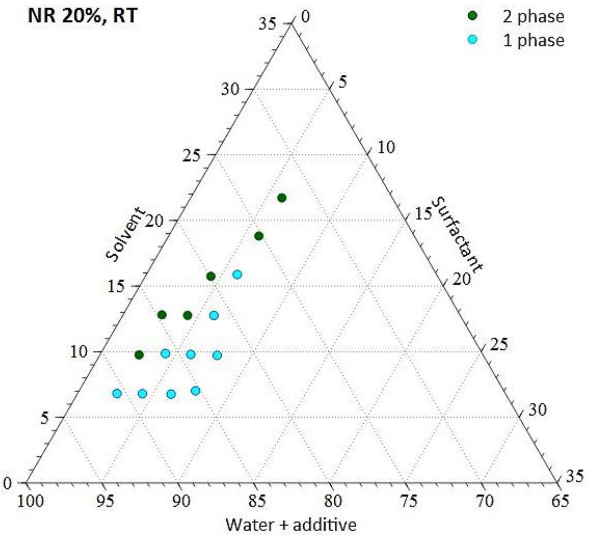
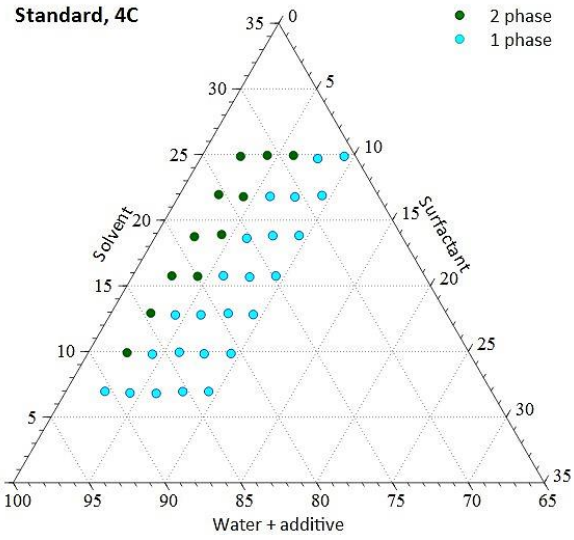


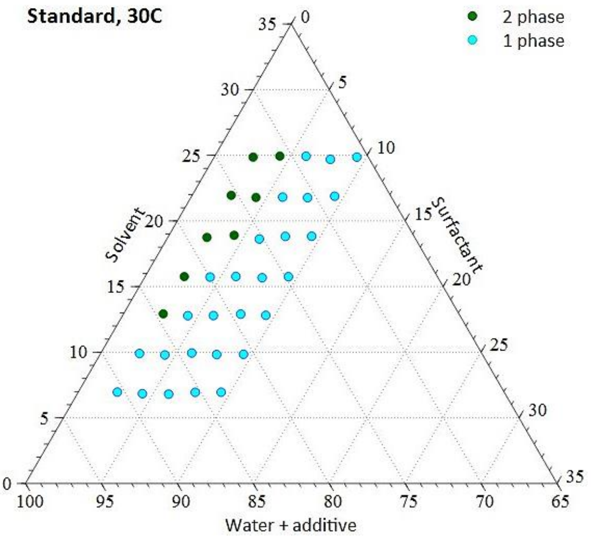
FIGURE 29. PHASE DIAGRAM FROM ANDERSSON [14] OF THE STANDARD SYSTEM.

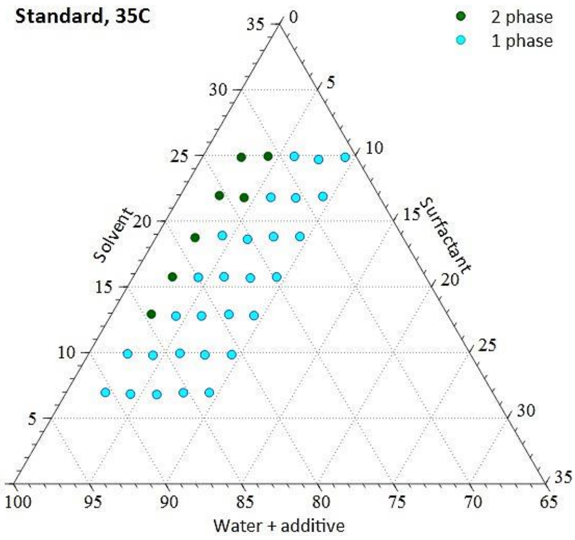
TABLE 10. STRIPPING TIMES OF THE STANDARD SYSTEM AS OBSERVED BY ANDERSSON [14].

	5 wt% S1	8 wt% S1	11 wt% S1	14 wt% S1	17 wt% S1
26 wt% Oil	-	-	6.5	8.25	9.5
23 wt% Oil	-	-	7.5	9.75	11.75
20 wt% Oil	-	-	7.75	11.75	16
17 wt% Oil	-	6.75	11	14.75	28.25
14 wt% Oil	-	10	16.75	28.25	73.75

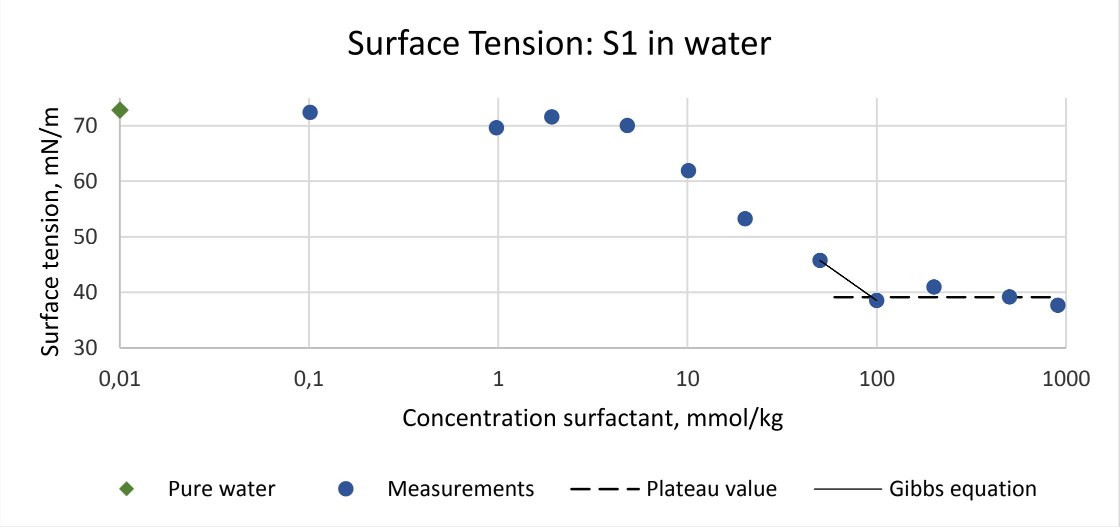

NR 20%, RT

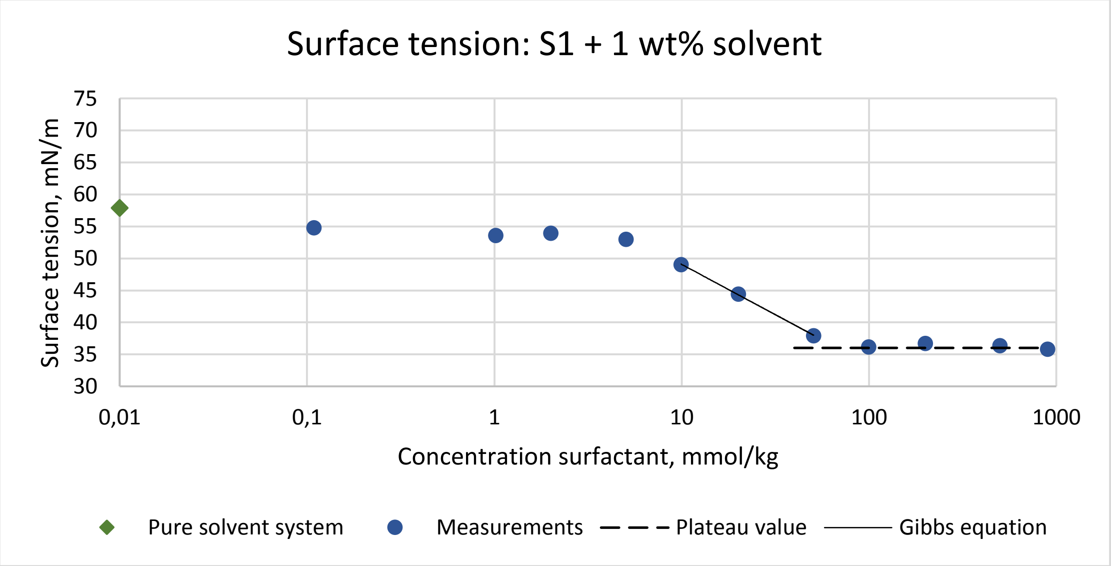

Standard, 4C

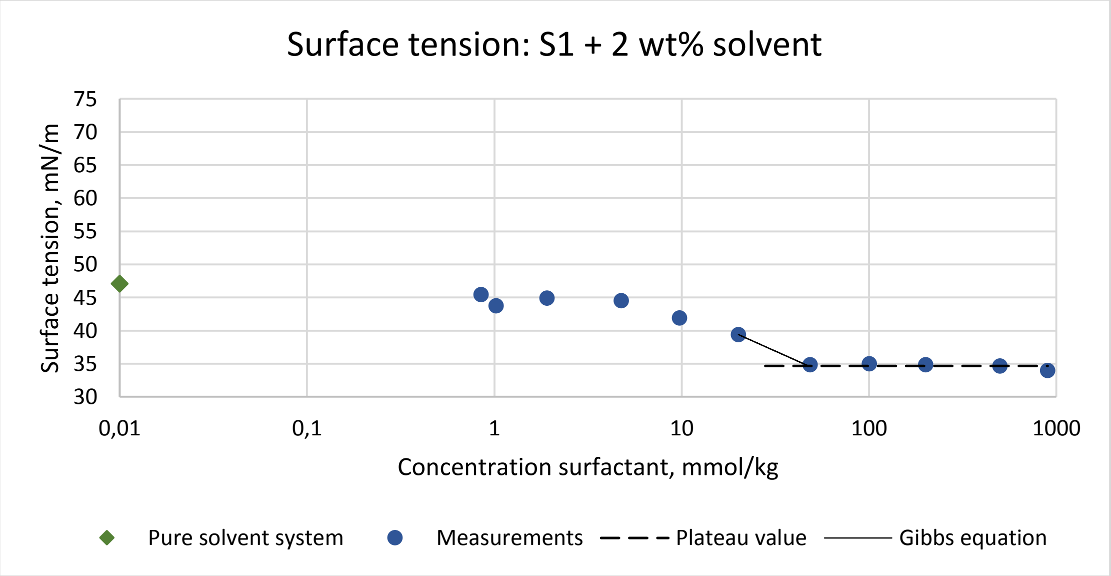

Standard, 30C

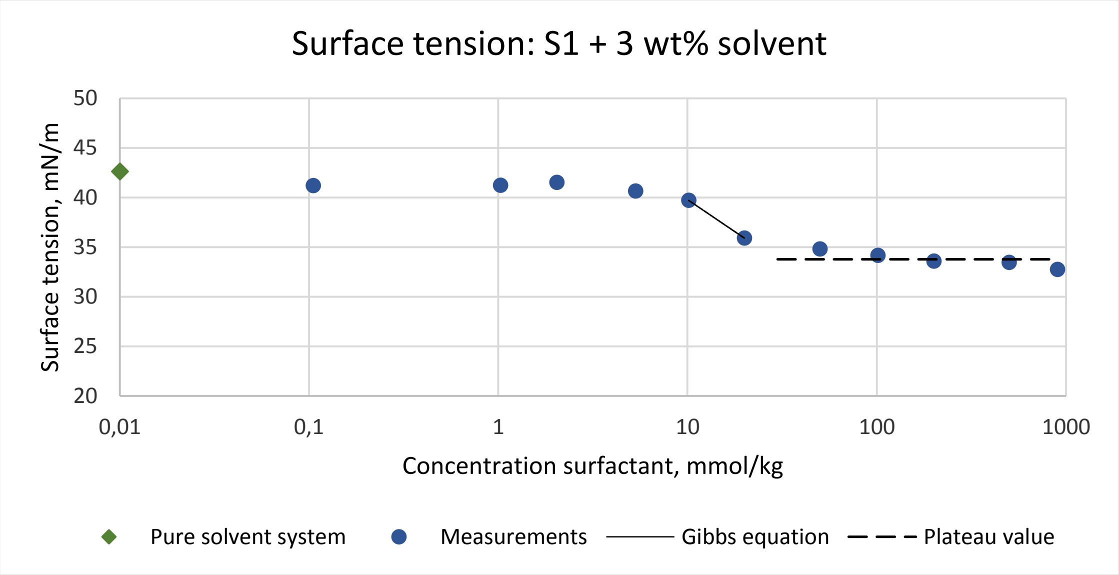

Standard, 35C

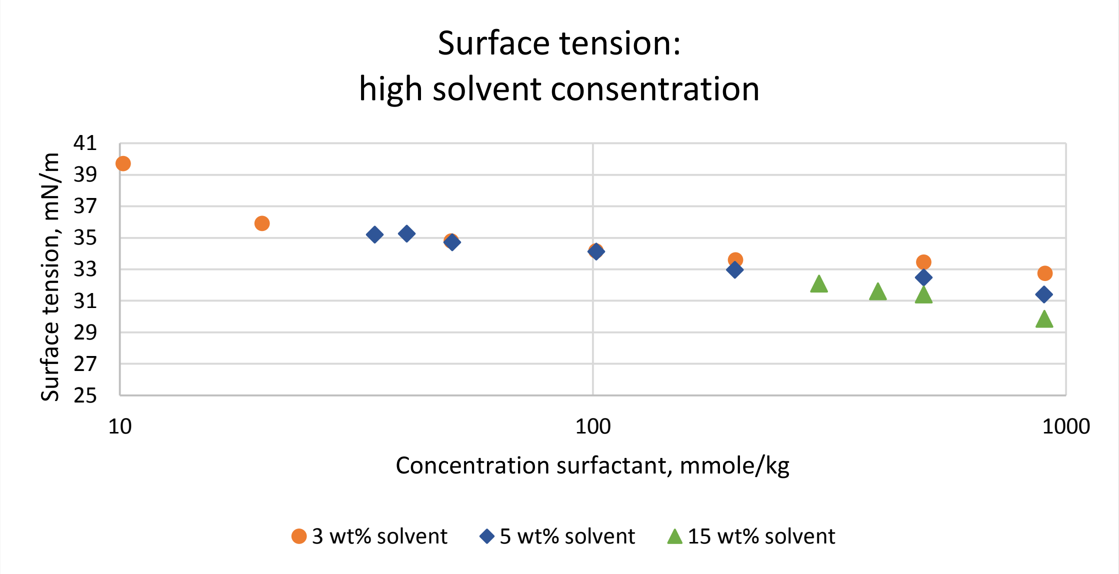
II. SURFACE TENSION MEASUREMENTS AND FITTING OF GIBBS EQUATION

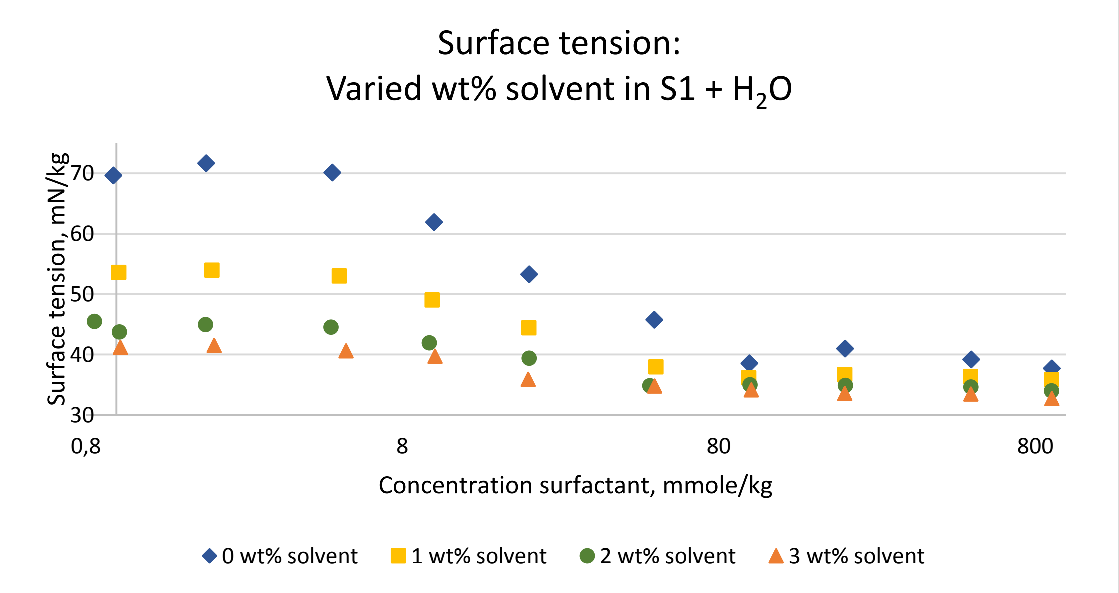


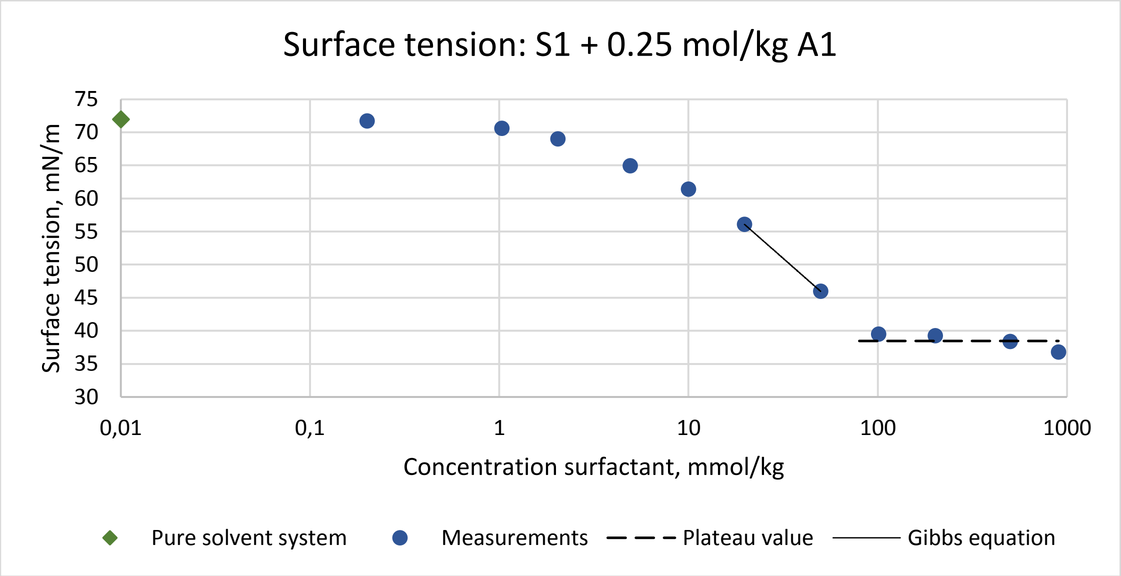


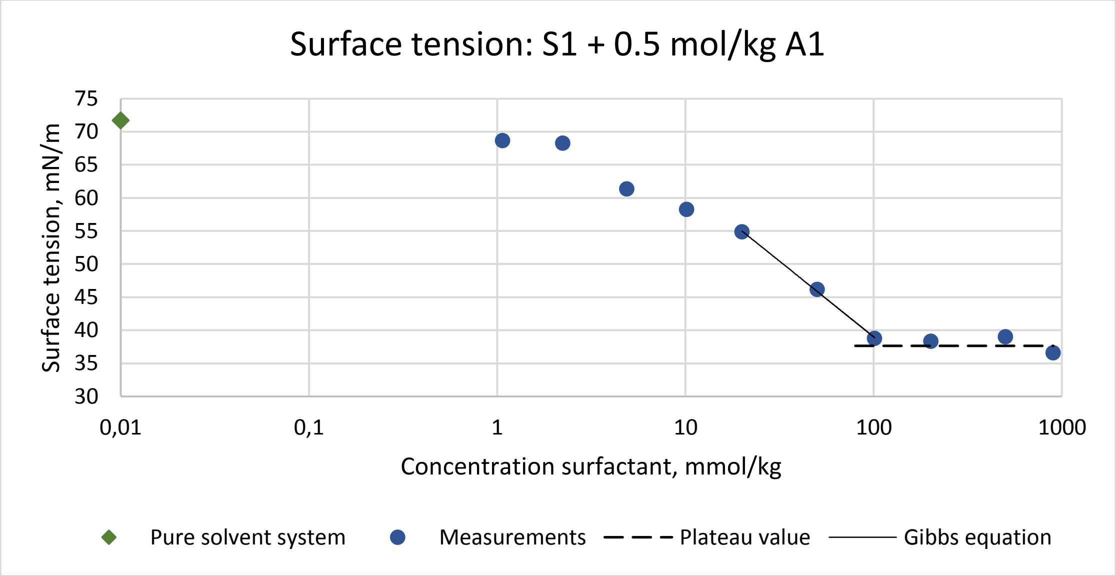


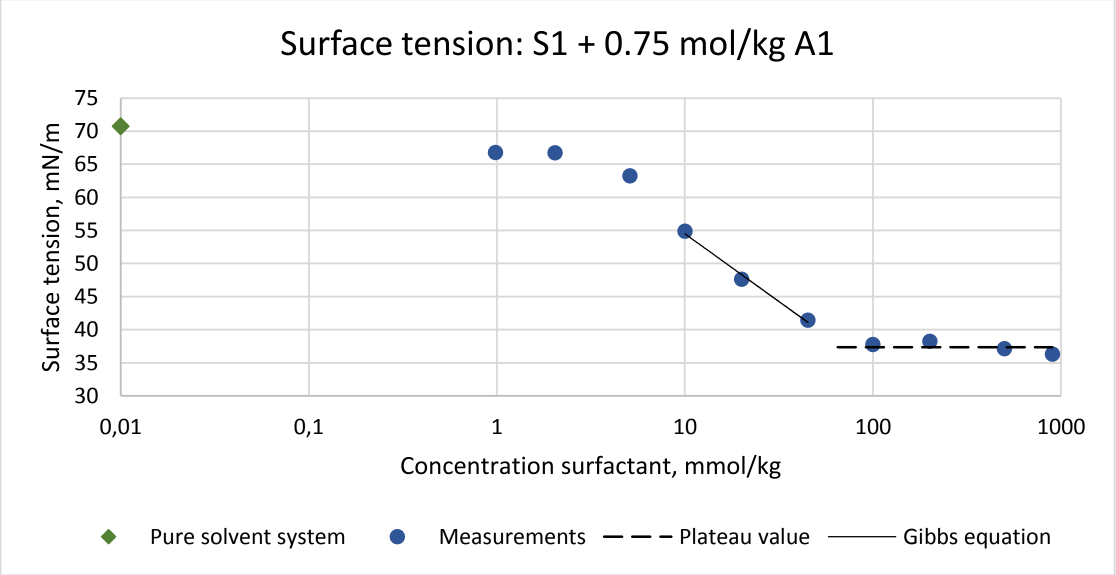

Surface tension: S1 + 3 wt% solvent
Surface tension, mN/m
50
45
40
35
30
25
20
0,01
0,1
1
10
100
1000
Concentration surfactant, mmol/kg
Pure solvent system
Measurements
Gibbs equation
Plateau value

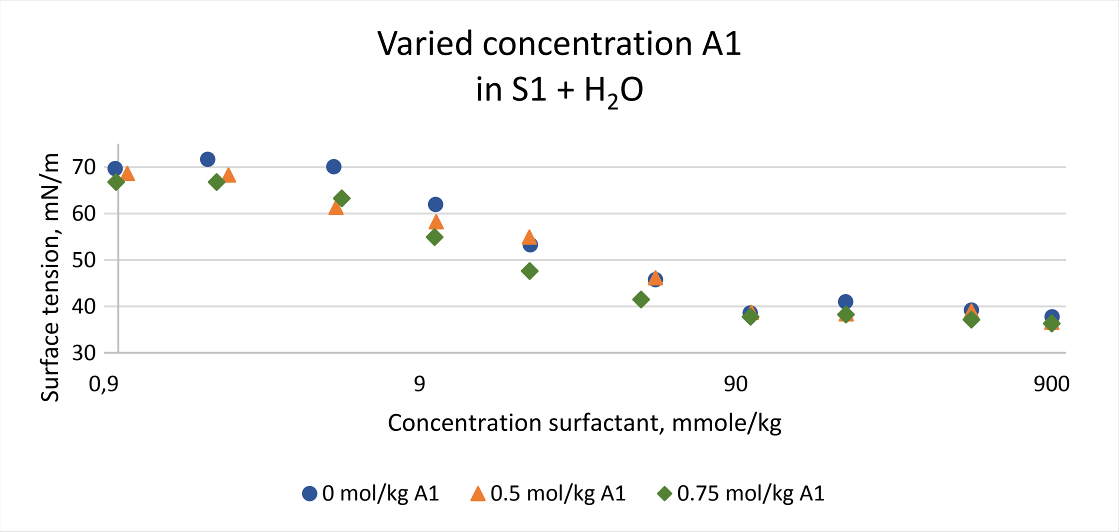

Surface tension:
high solvent consentration
Surface tension, mN/m
41
39
37
35
33
31
29
27
25
10
100
1000
Concentration surfactant, mmole/kg
3 wt% solvent
5 wt% solvent
15 wt% solvent

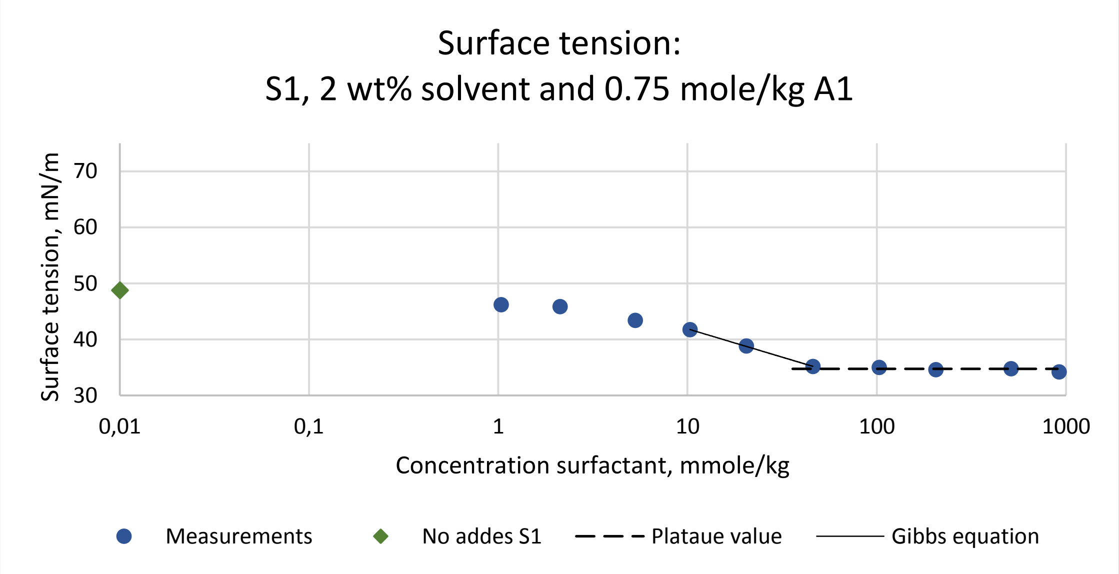

Surface tension:
Varied wt% solvent in S1 + H2O
Surface tension, mN/kg
70
60
50
40
30
0,8
8
80
800
Concentration surfactant, mmole/kg
0 wt% solvent
1 wt% solvent
2 wt% solvent
3 wt% solvent

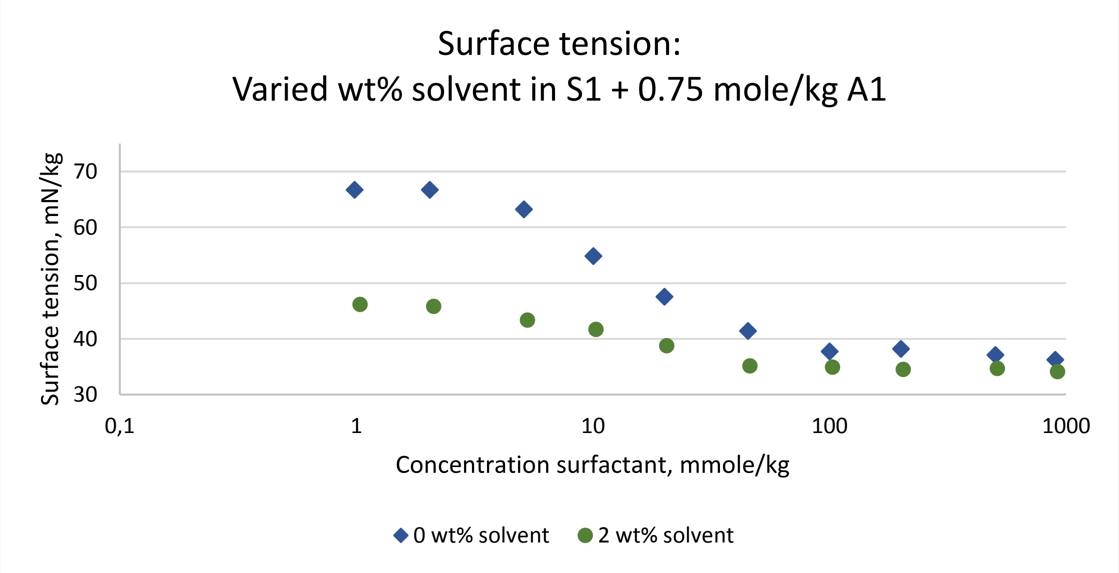

Surface tension: S1 + 0.25 mol/kg A1
Surface tension, mN/m
75
70
65
60
55
50
45
40
35
30
0,01
0,1
1
10
100
1000
Concentration surfactant, mmol/kg
Pure solvent system
Measurements
Plateau value
Gibbs equation

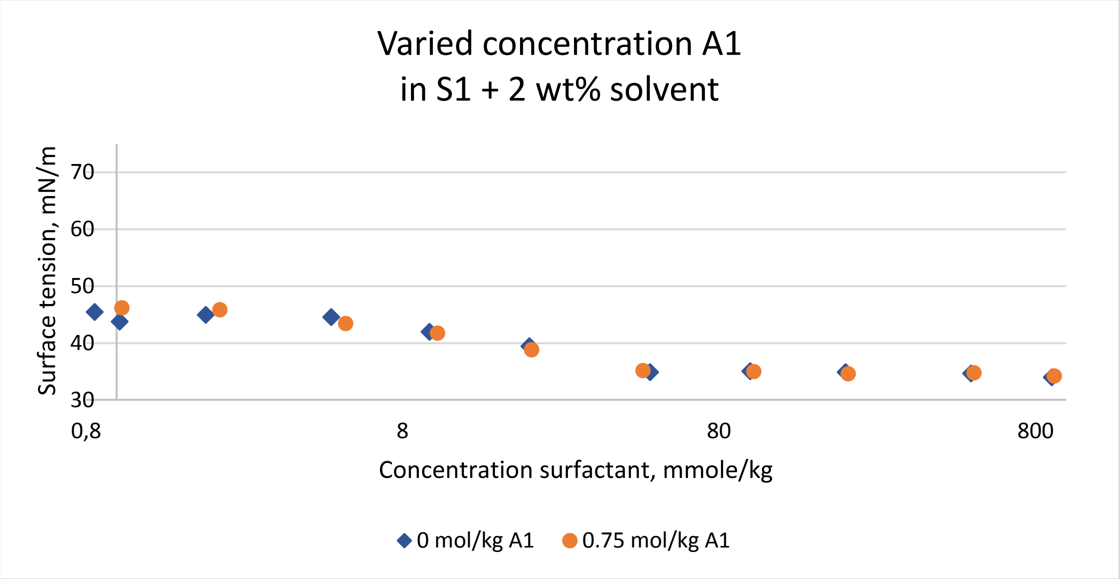

Surface tension: S1 + 0.5 mol/kg A1
Surface tension, mN/m
75
70
65
60
55
50
45
40
35
30
0,01
0,1
1
10
100
1000
Concentration surfactant, mmol/kg
Pure solvent system
Measurements
Plateau value
Gibbs equation

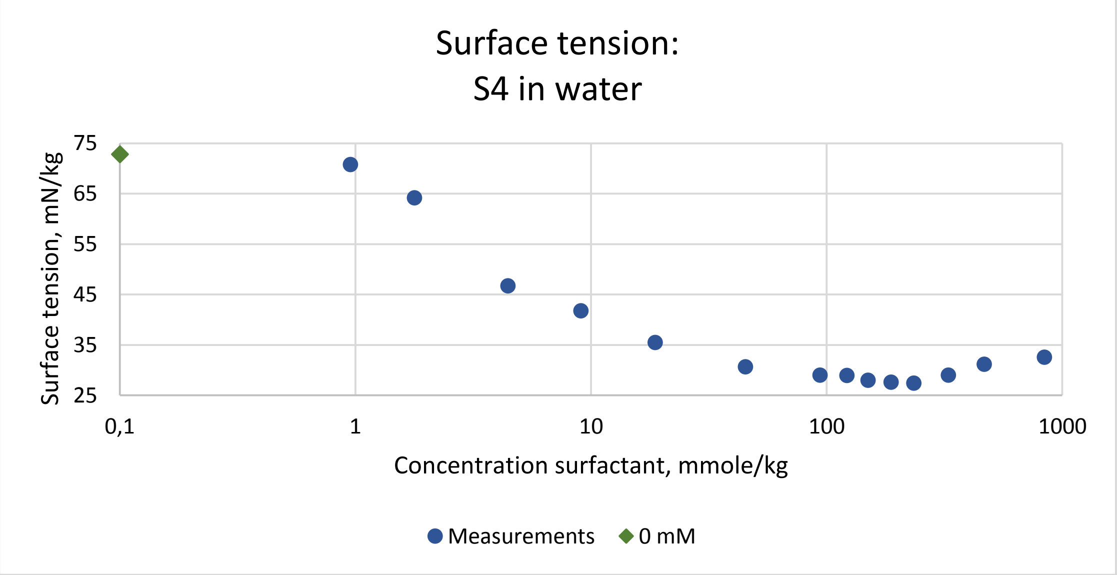

Surface tension: S1 + 0.75 mol/kg A1
Surface tension, mN/m
75
70
65
60
55
50
45
40
35
30
0,01
0,1
1
10
100
1000
Concentration surfactant, mmol/kg
Pure solvent system
Measurements
Plateau value
Gibbs equation

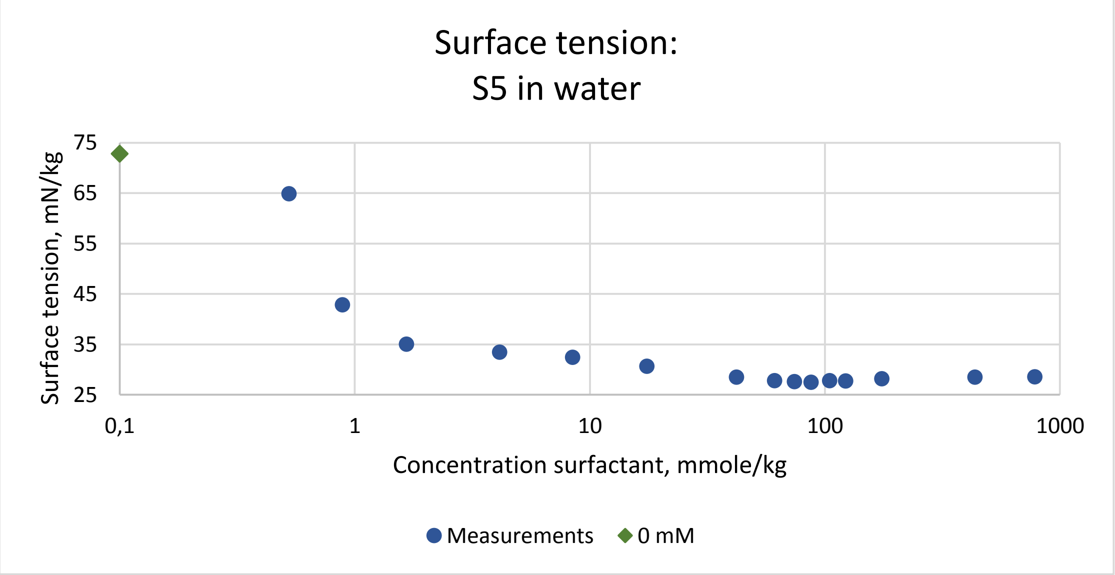

Varied concentration A1
in S1 + H_2O
Surface tension, mN/m
70
60
50
40
30
0,9
9
90
900
Concentration surfactant, mmole/kg
● 0 mol/kg A1
▲ 0.5 mol/kg A1
◆ 0.75 mol/kg A1


Surface tension:
S1, 2 wt% solvent and 0.75 mole/kg A1
Surface tension, mN/m
70
60
50
40
30
0,01
0,1
1
10
100
1000
Concentration surfactant, mmole/kg
● Measurements
◆ No addes S1
– – – Plataue value
—— Gibbs equation

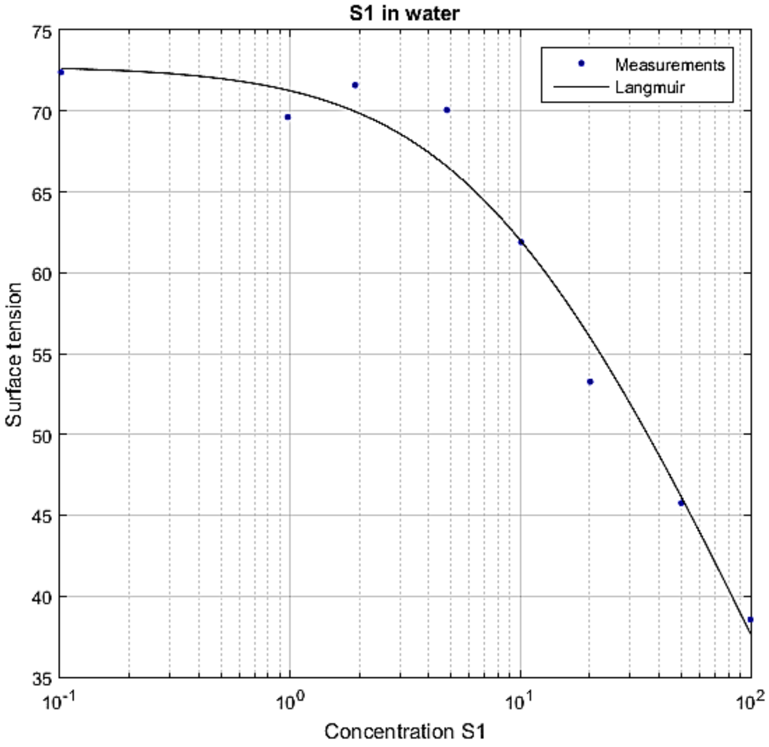

Surface tension:
Varied wt% solvent in S1 + 0.75 mole/kg A1
Surface tension, mN/kg
70
60
50
40
30
0,1
1
10
100
1000
Concentration surfactant, mmole/kg
◆ 0 wt% solvent
● 2 wt% solvent

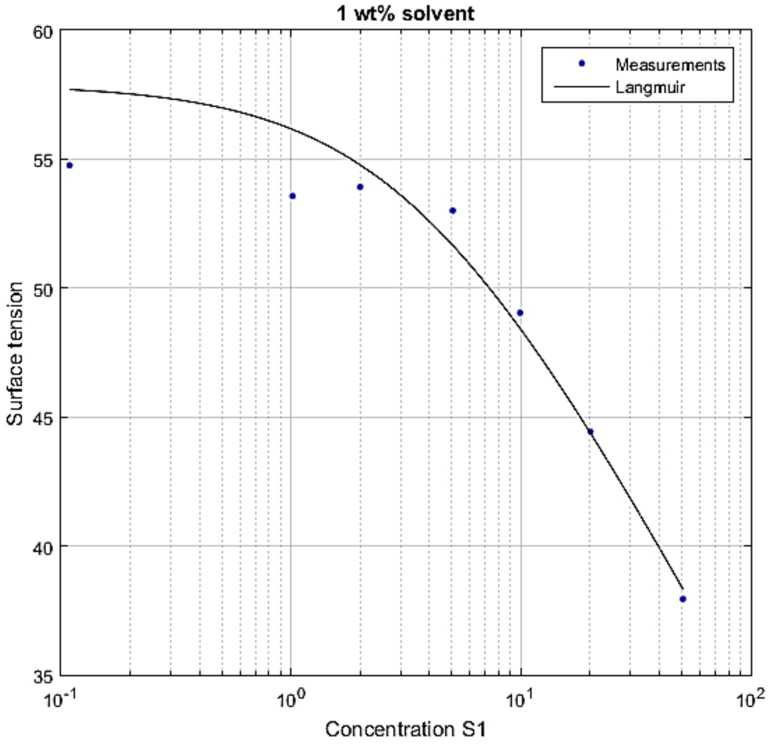

Varied concentration A1
in S1 + 2 wt% solvent
Surface tension, mN/m
70
60
50
40
30
0,8
8
80
800
Concentration surfactant, mmole/kg
◆ 0 mol/kg A1
● 0.75 mol/kg A1

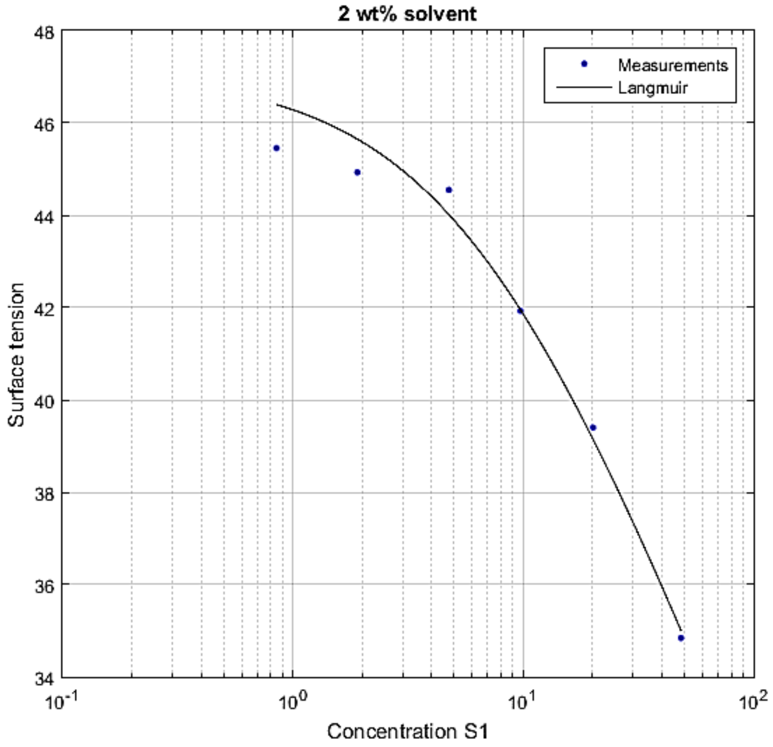

Surface tension:
S4 in water
Surface tension, mN/kg
75
65
55
45
35
25
0,1
1
10
100
1000
Concentration surfactant, mmole/kg
● Measurements
◆ 0 mM

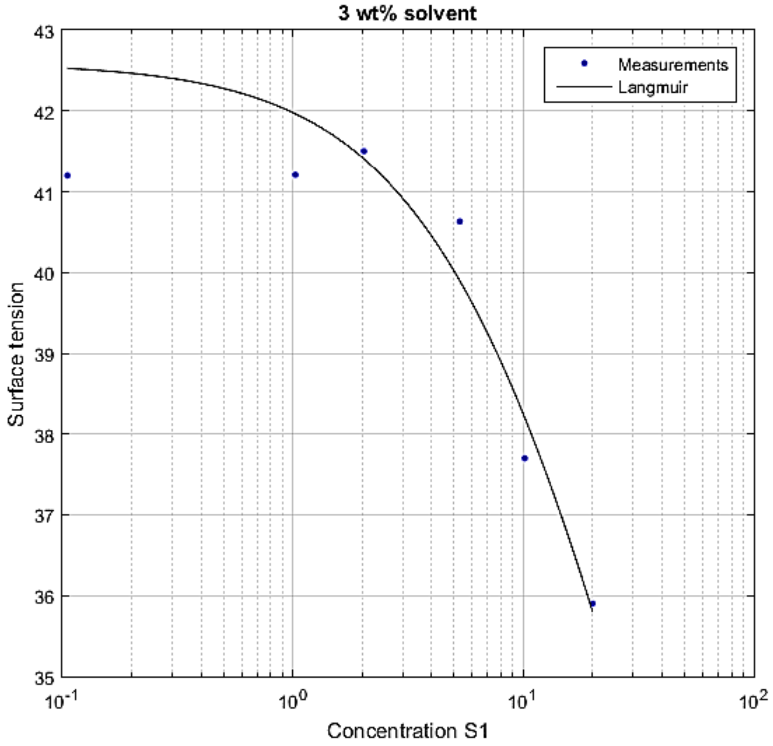

Surface tension:
S5 in water
Surface tension, mN/kg
75
65
55
45
35
25
0,1
1
10
100
1000
Concentration surfactant, mmole/kg
● Measurements
◆ 0 mM

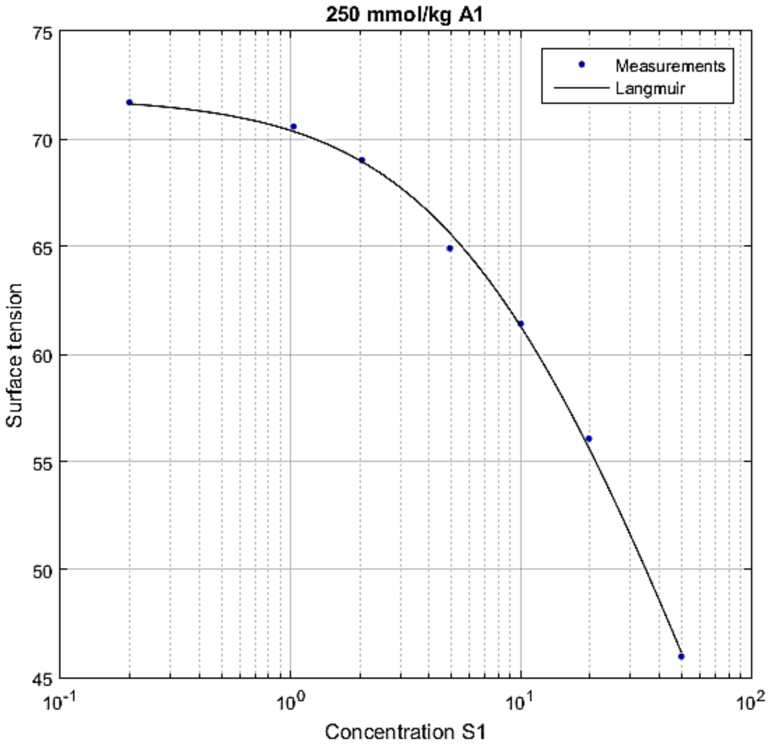
III. SURFACE TENSION MEASUREMENTS AND FITTING OF THE LANGMUIR EQUATION

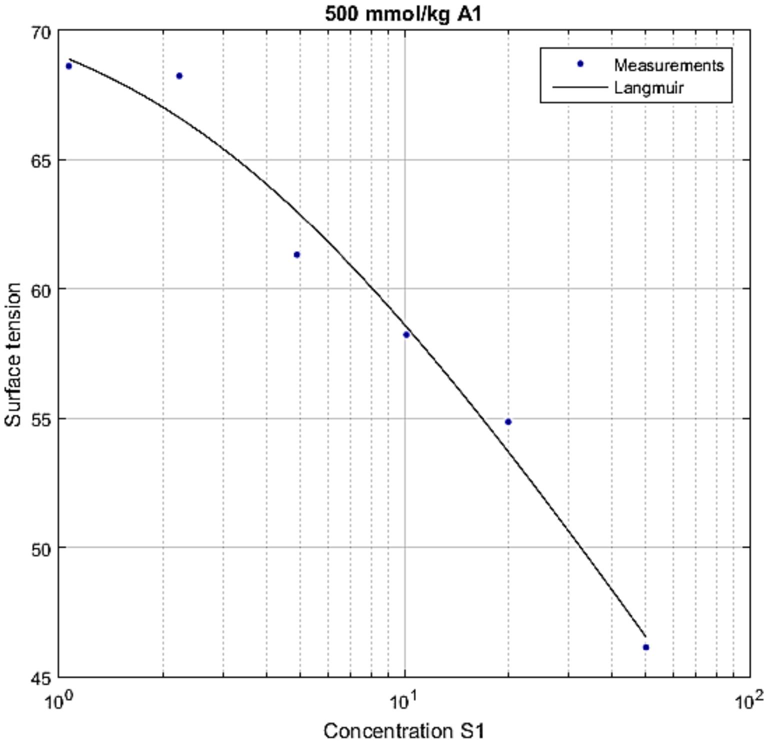


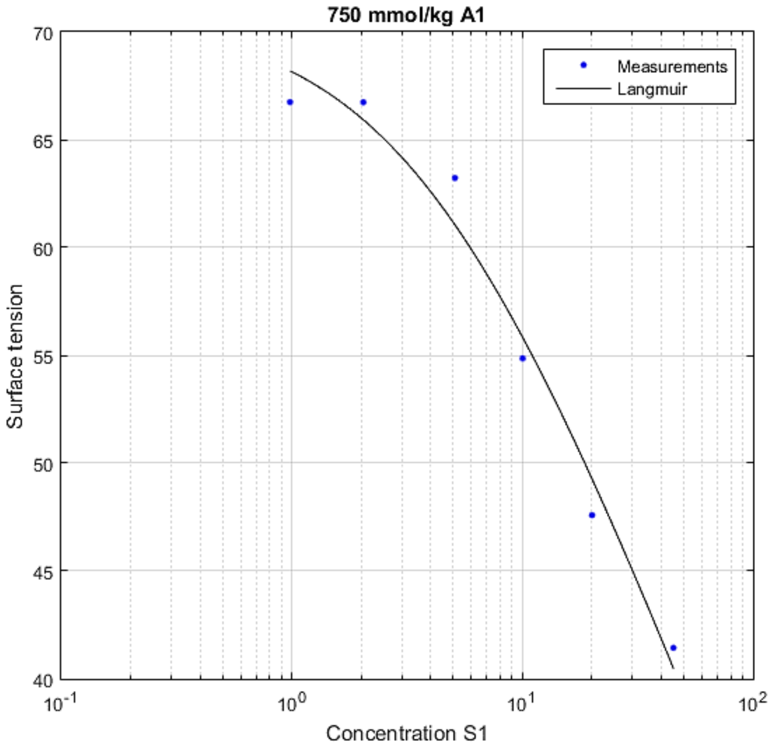


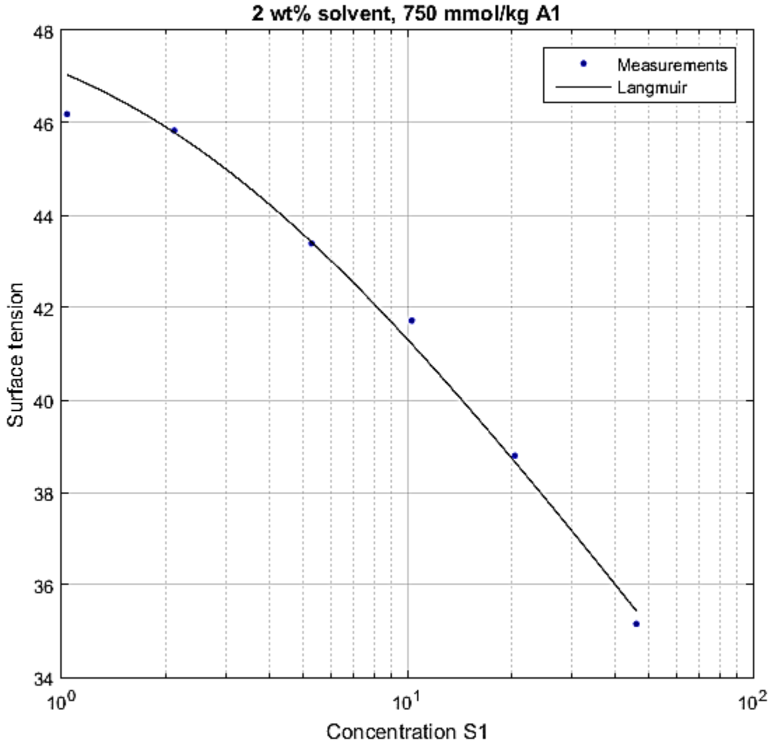

2 wt% solvent
Surface tension
48
46
44
42
40
38
36
34
10^{-1}
10^{0}
10^{1}
10^{2}
Concentration S1
Measurements
Langmuir


3 wt% solvent
Surface tension
43
42
41
40
39
38
37
36
35
10^{-1}
10^{0}
10^{1}
10^{2}
Concentration S1
Measurements
Langmuir

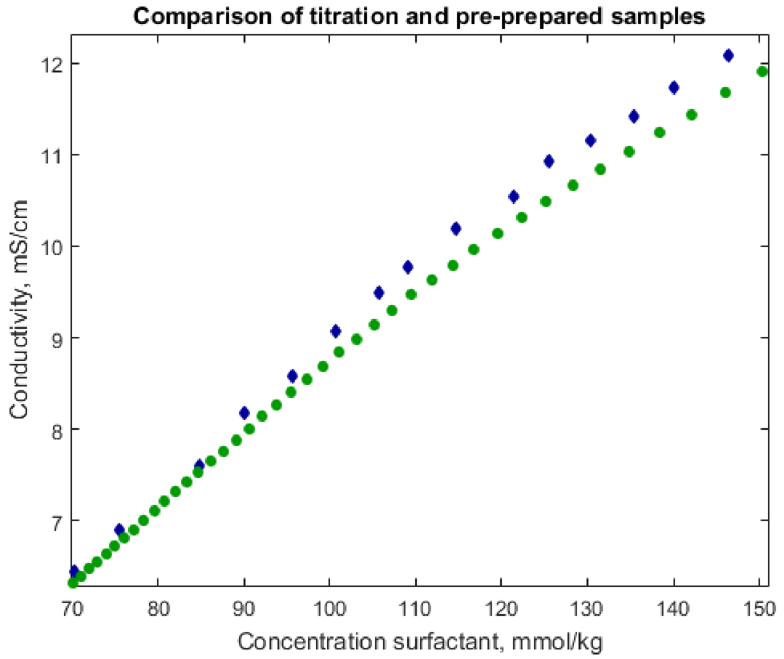

250 mmol/kg A1
Measurements
Langmuir
Surface tension
Concentration S1
75
70
65
60
55
50
45
10^{-1}
10^{0}
10^{1}
10^{2}

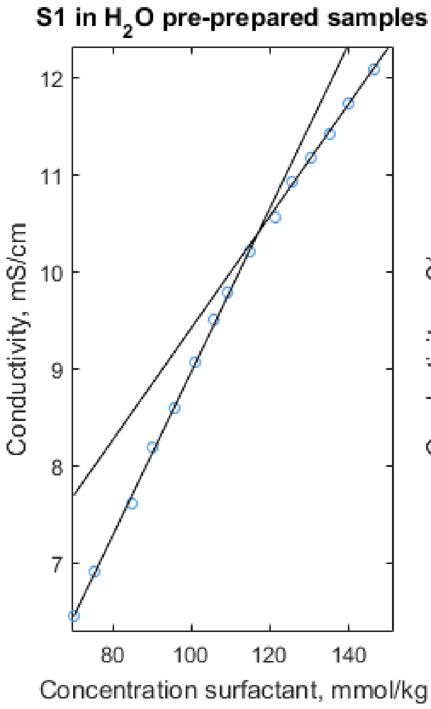

500 mmol/kg A1
Measurements
Langmuir
Surface tension
Concentration S1
70
65
60
55
50
45
10^{0}
10^{1}
10^{2}

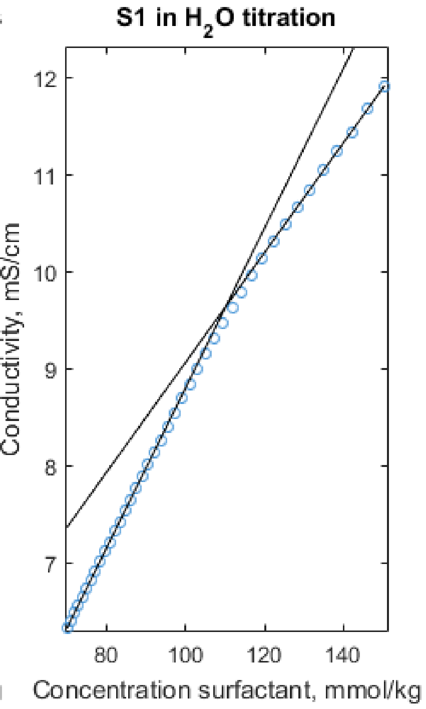

750 mmol/kg A1
Measurements
Langmuir
Surface tension
70
65
60
55
50
45
40
10^{-1}
10^{0}
10^{1}
10^{2}
Concentration S1

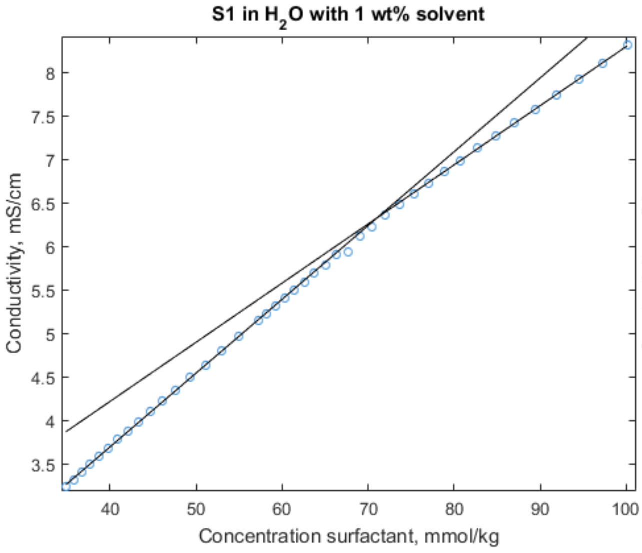

2 wt% solvent, 750 mmol/kg A1
Measurements
Langmuir
Surface tension
48
46
44
42
40
38
36
34
10^{0}
10^{1}
10^{2}
Concentration S1

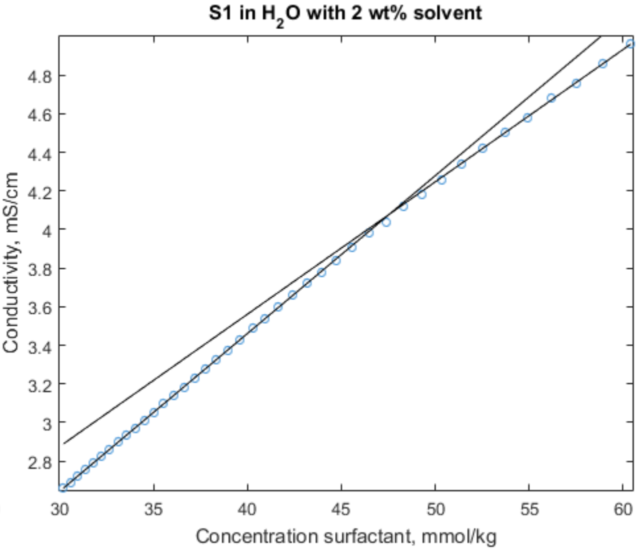
IV. CONDUCTIVITY

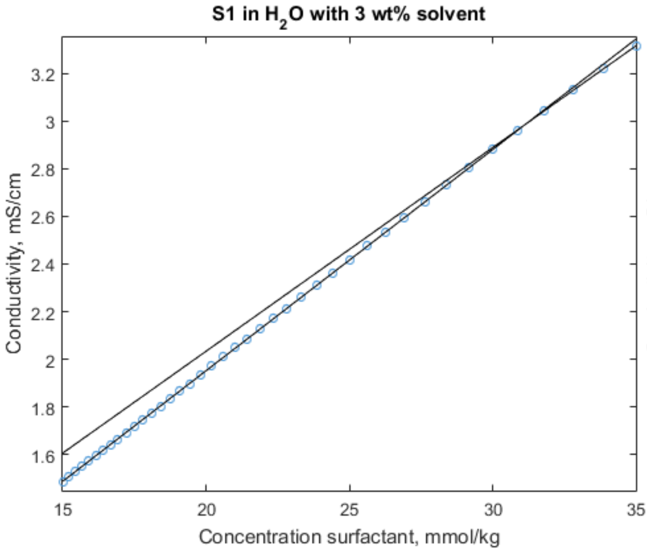


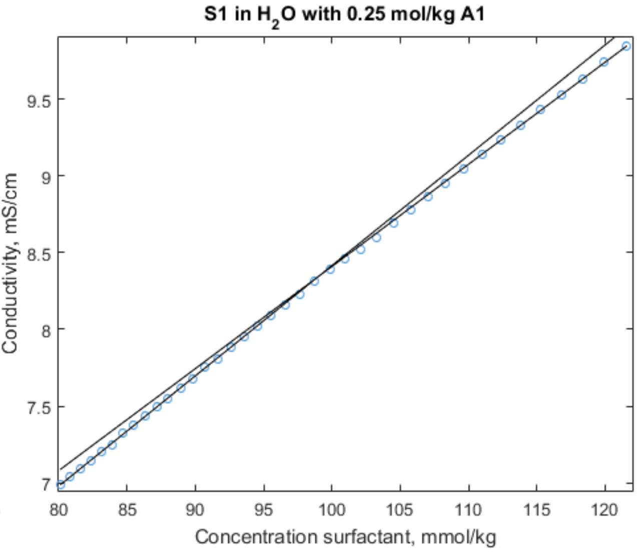


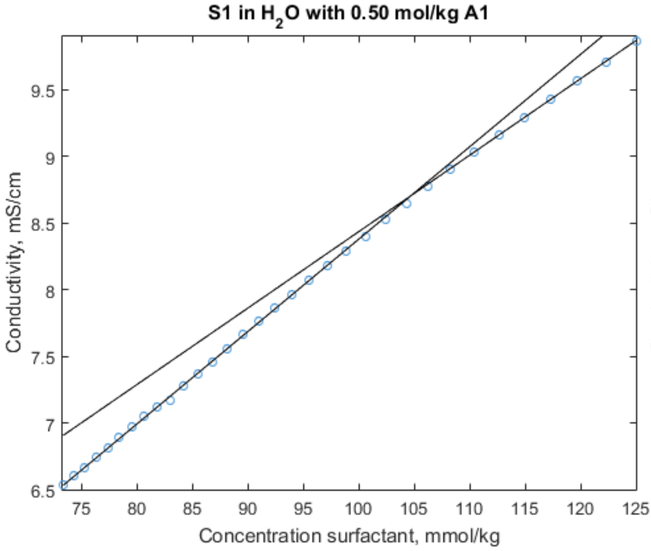


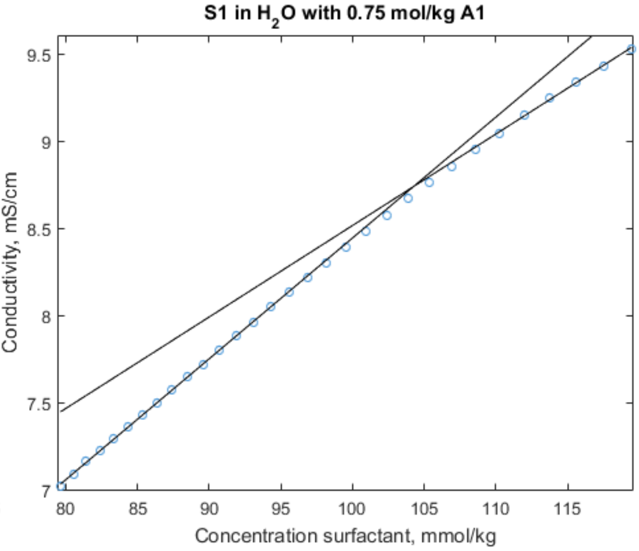

S1 in H_2O with 1 wt% solvent

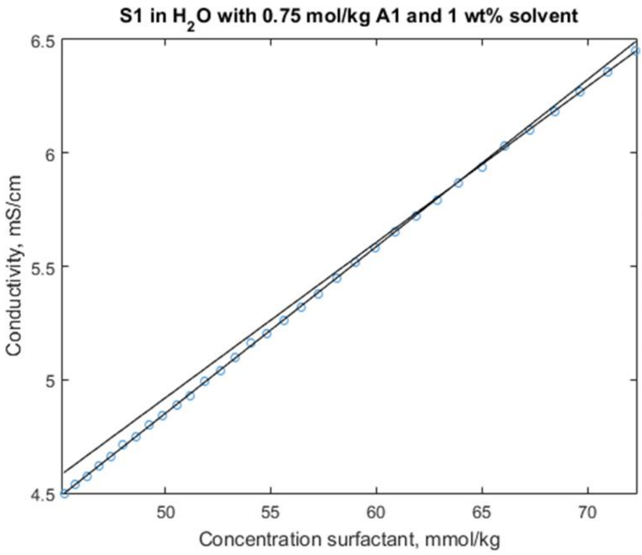

S1 in H_2O with 2 wt% solvent


S1 in H_2O with 3 wt% solvent

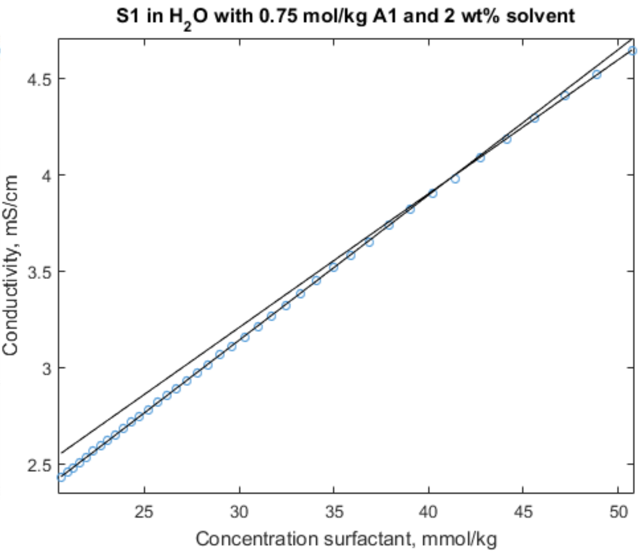

S1 in H_2O with 0.25 mol/kg A1


S1 in H_2O with 0.50 mol/kg A1


S1 in H_2O with 0.75 mol/kg A1

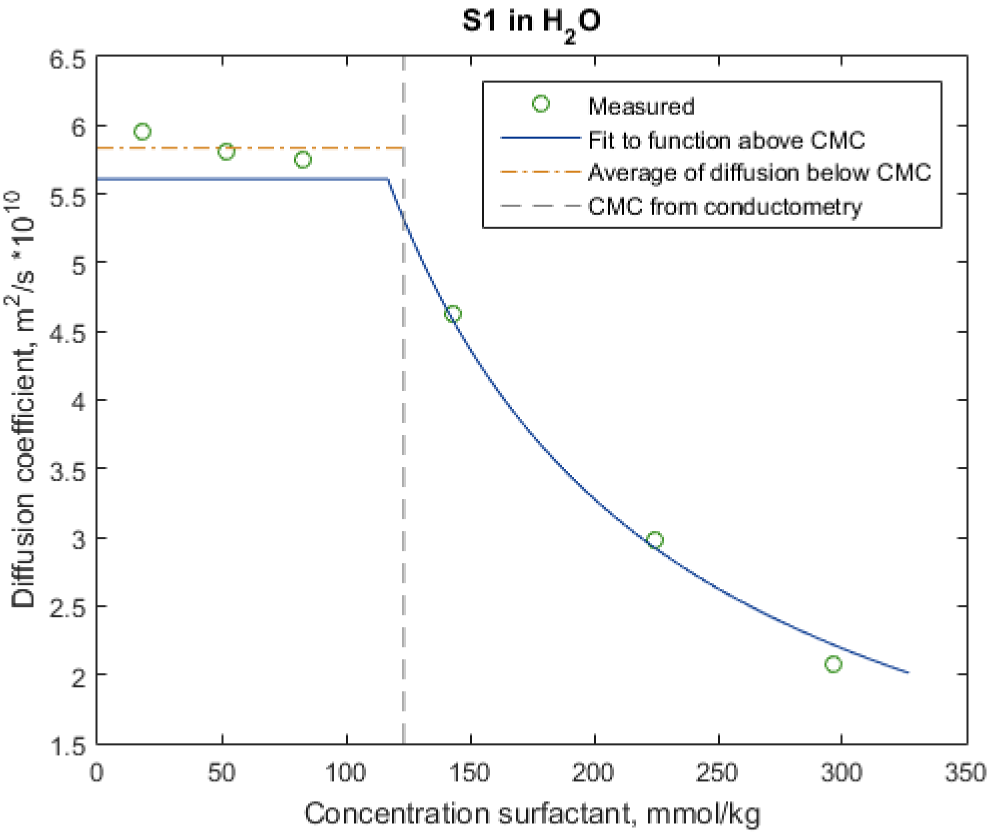


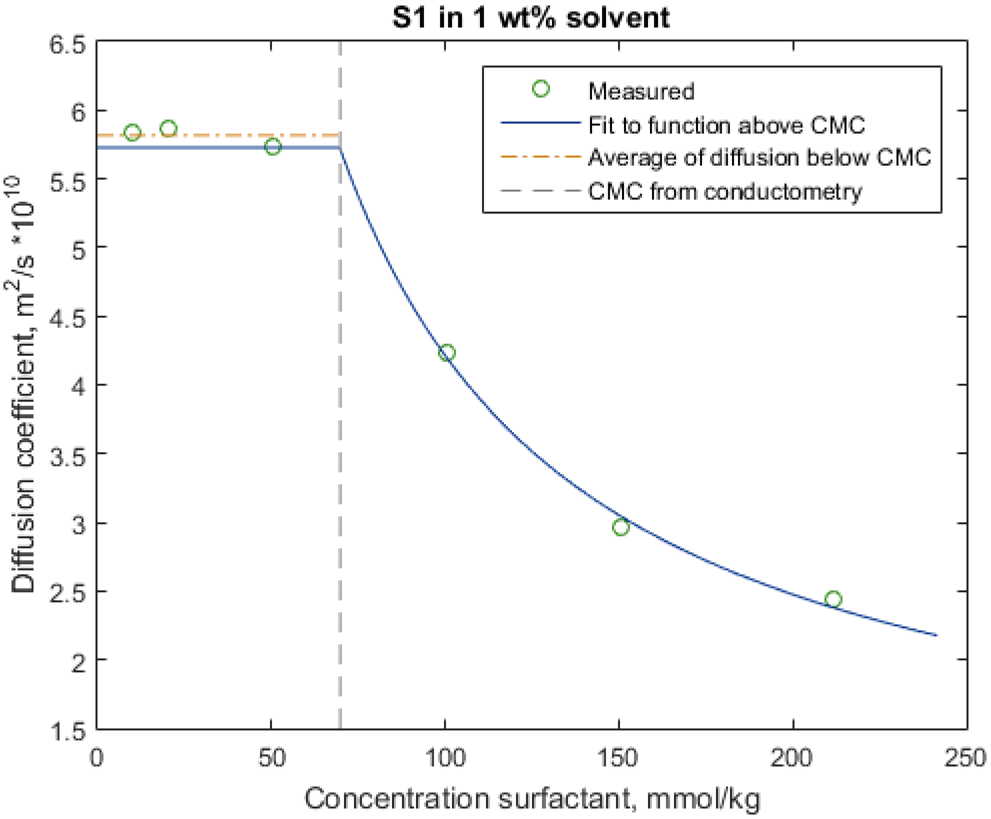
S1 in H_2O with 0.75 mol/kg A1 and 1 wt% solvent

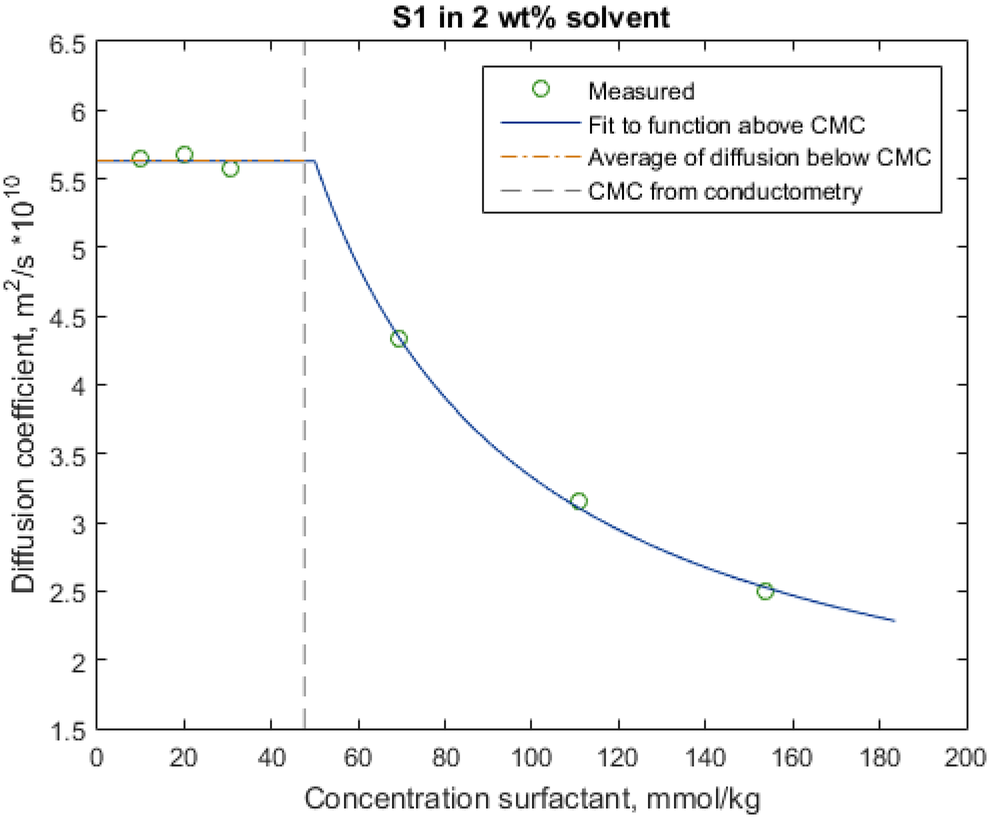


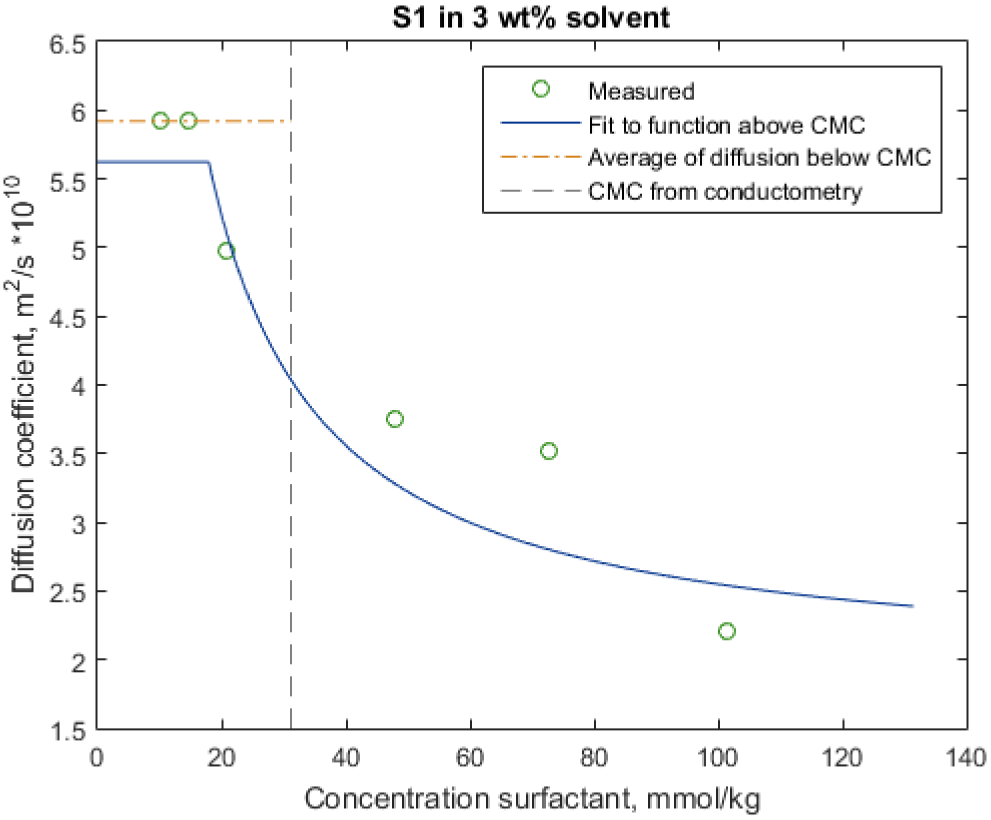
S1 in H_2O with 0.75 mol/kg A1 and 2 wt% solvent

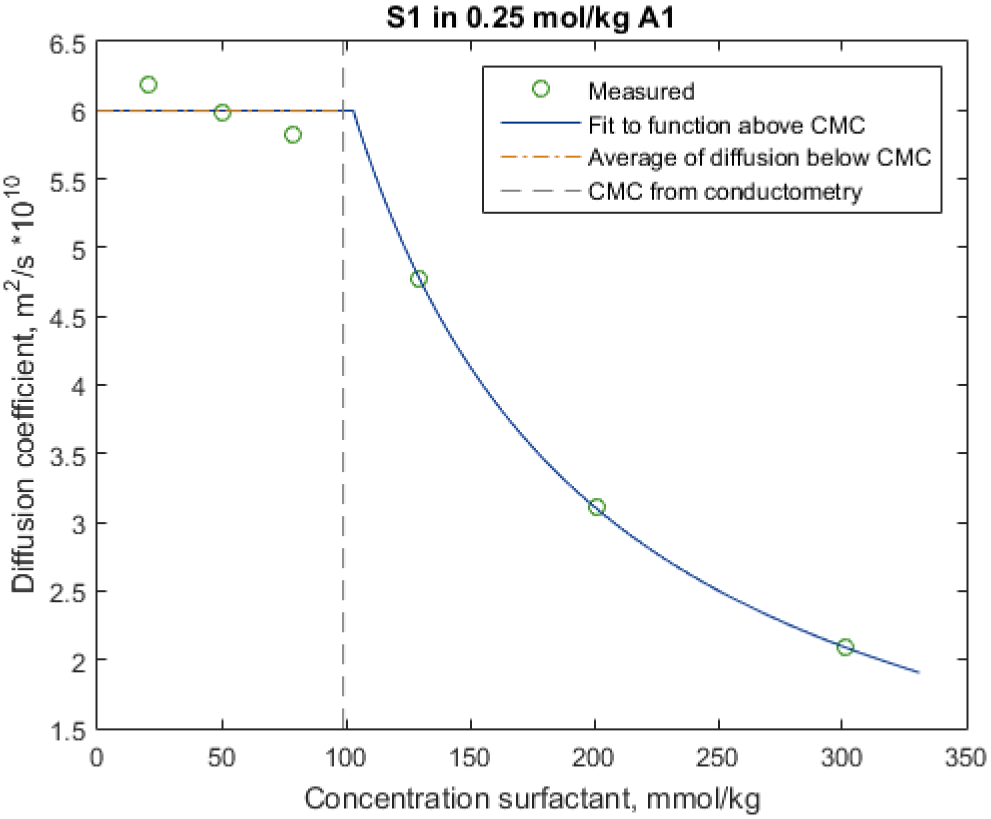
V. DIFFUSION

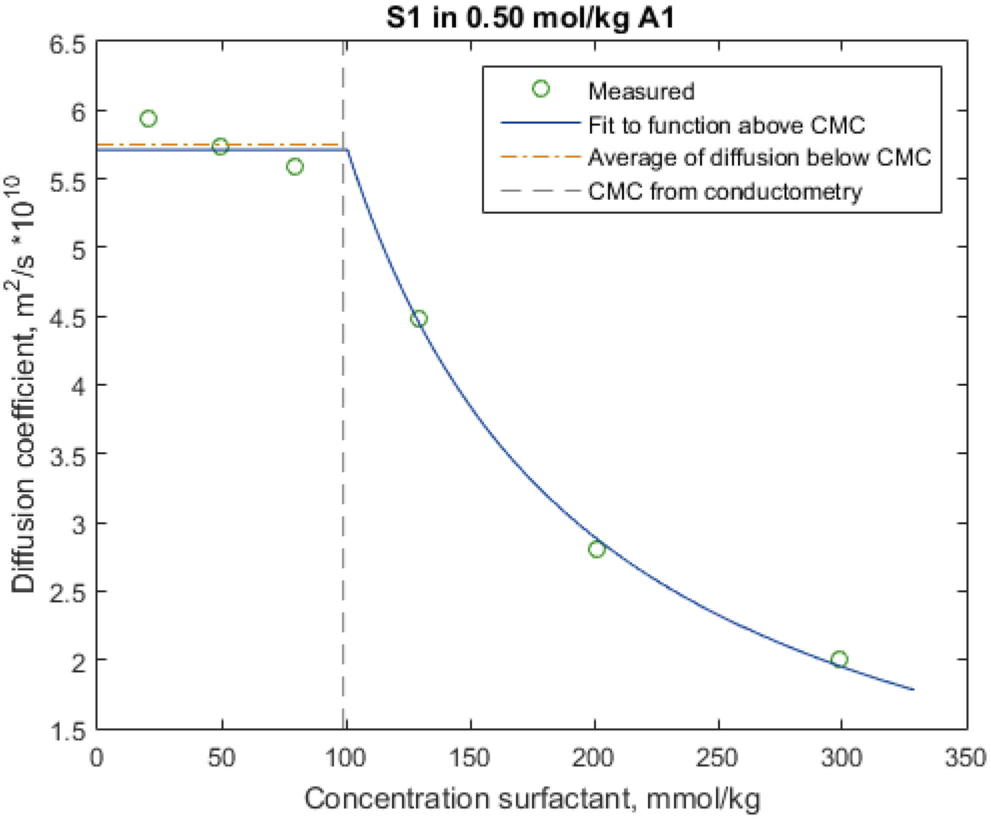

S1 in H_2O
Diffusion coefficient, m²/s *10¹⁰
Concentration surfactant, mmol/kg
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
0
50
100
150
200
250
300
350
Measured
Fit to function above CMC
Average of diffusion below CMC
CMC from conductometry

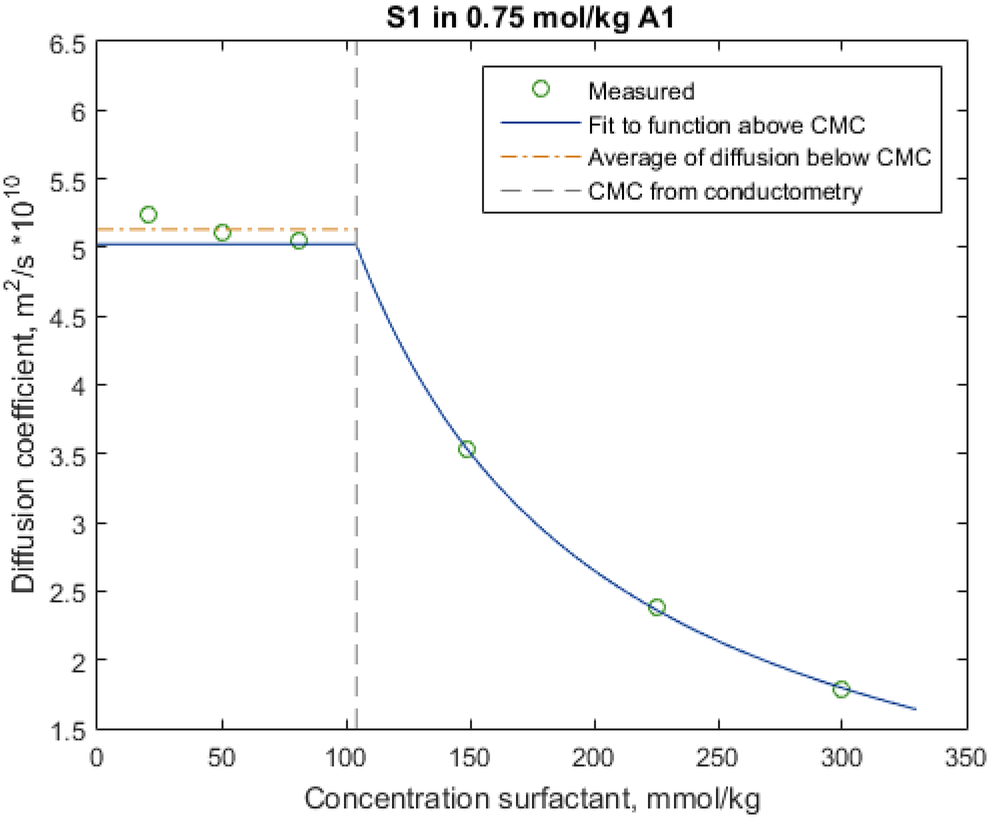

S1 in 1 wt% solvent
Diffusion coefficient, m²/s *10¹⁰
Concentration surfactant, mmol/kg
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
0
50
100
150
200
250
Measured
Fit to function above CMC
Average of diffusion below CMC
CMC from conductometry

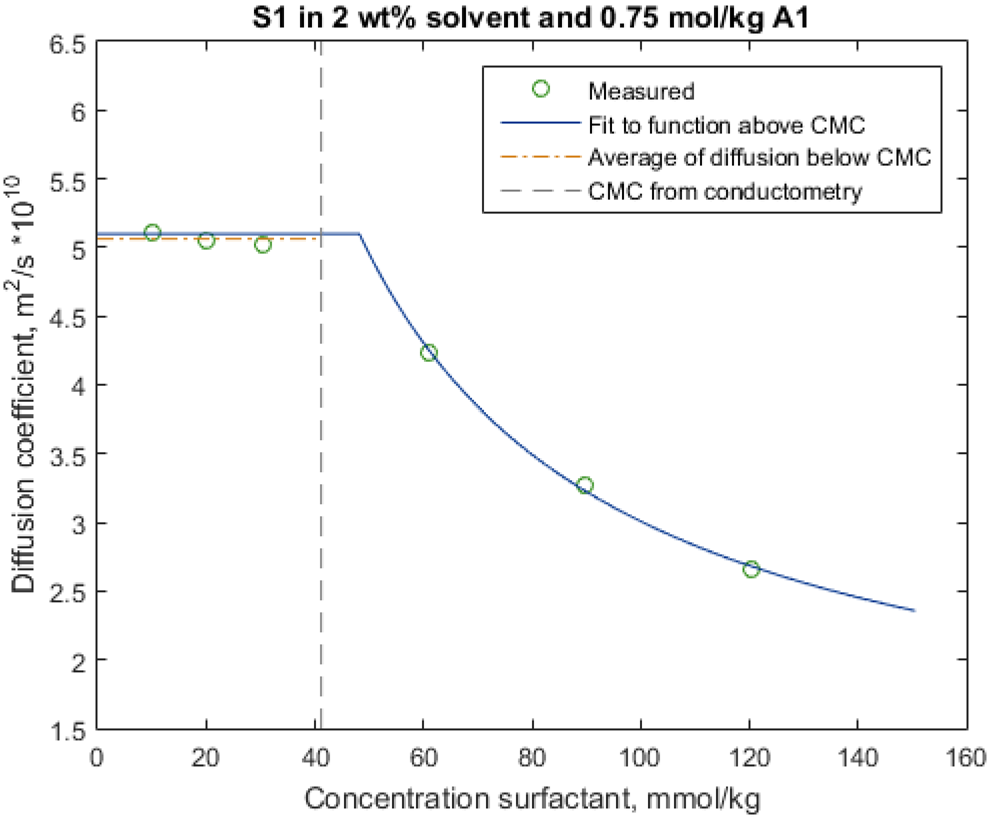

S1 in 2 wt% solvent
Measured
Fit to function above CMC
Average of diffusion below CMC
CMC from conductometry
Diffusion coefficient, m^2/s *10^{10}
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
0
20
40
60
80
100
120
140
160
180
200
Concentration surfactant, mmol/kg

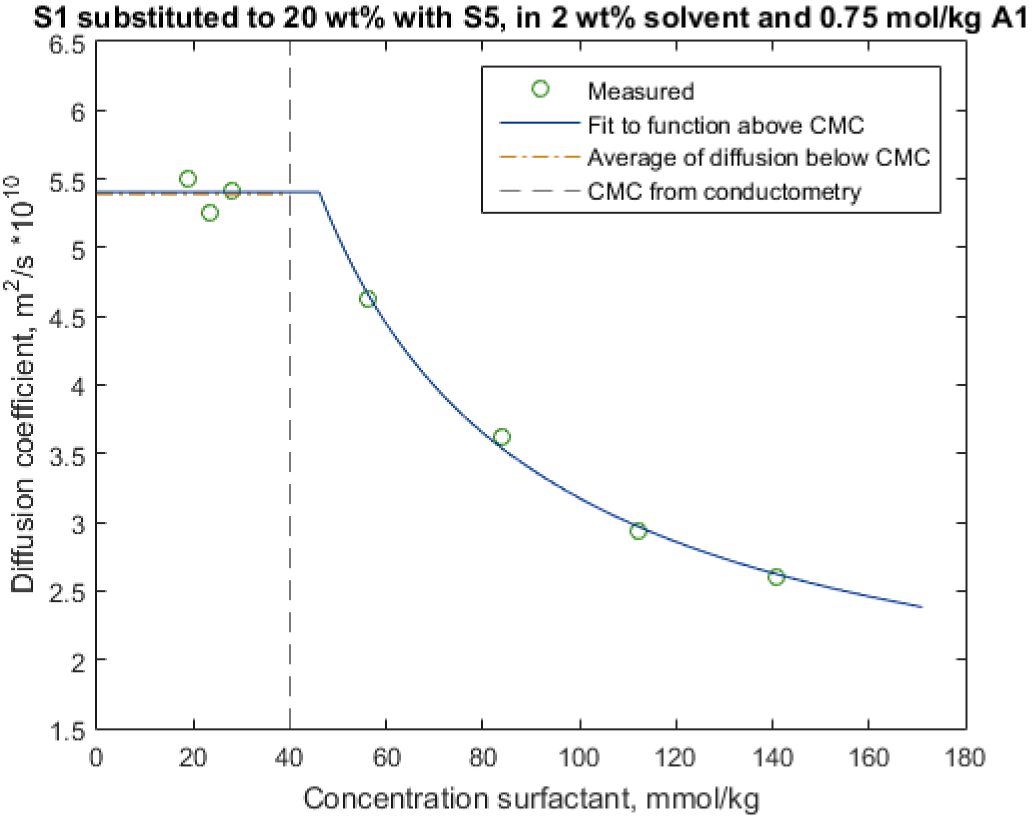

S1 in 3 wt% solvent
Measured
Fit to function above CMC
Average of diffusion below CMC
CMC from conductometry
Diffusion coefficient, m^2/s *10^{10}
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
0
20
40
60
80
100
120
140
Concentration surfactant, mmol/kg


S1 in 0.25 mol/kg A1
Measured
Fit to function above CMC
Average of diffusion below CMC
CMC from conductometry
Diffusion coefficient, m^2/s *10^{10}
Concentration surfactant, mmol/kg
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
0
50
100
150
200
250
300
350


S1 in 0.50 mol/kg A1
Measured
Fit to function above CMC
Average of diffusion below CMC
CMC from conductometry
Diffusion coefficient, m^2/s *10^{10}
Concentration surfactant, mmol/kg
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
0
50
100
150
200
250
300
350


S1 in 0.75 mol/kg A1
Measured
Fit to function above CMC
Average of diffusion below CMC
CMC from conductometry
Diffusion coefficient, m^2/s *10^{10}
Concentration surfactant, mmol/kg
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
0
50
100
150
200
250
300
350


S1 in 2 wt% solvent and 0.75 mol/kg A1
Measured
Fit to function above CMC
Average of diffusion below CMC
CMC from conductometry
Diffusion coefficient, m^2/s *10^{10}
Concentration surfactant, mmol/kg
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
0
20
40
60
80
100
120
140
160


S1 substituted to 20 wt% with S5, in 2 wt% solvent and 0.75 mol/kg A1
Measured
Fit to function above CMC
Average of diffusion below CMC
CMC from conductometry
Diffusion coefficient, m^2/s *10^{10}
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
0
20
40
60
80
100
120
140
160
180
Concentration surfactant, mmol/kg